

## Microstructural and Oxidative Mechanical Wear Study on TiAlCN/VCN

KAMATH, G, EHIASARIAN, Arutiun <<http://orcid.org/0000-0001-6080-3946>>, PURANDARE, Yashodhan <<http://orcid.org/0000-0002-7544-9027>> and HOVSEPIAN, Papken <<http://orcid.org/0000-0002-1047-0407>>

Available from Sheffield Hallam University Research Archive (SHURA) at:

<http://shura.shu.ac.uk/23540/>

---

This document is the author deposited version. You are advised to consult the publisher's version if you wish to cite from it.

### Published version

KAMATH, G, EHIASARIAN, Arutiun, PURANDARE, Yashodhan and HOVSEPIAN, Papken (2010). Microstructural and Oxidative Mechanical Wear Study on TiAlCN/VCN. In: 53rd Annual Technical Conference, 17 Apr 2010 - 22 Apr 2010. Society of Vacuum Coaters.

---

### Copyright and re-use policy

See <http://shura.shu.ac.uk/information.html>

# Microstructural and oxidative mechanical wear study on TiAlCN/VCN nanoscale multilayer coating deposited by HIPIMS/(HIPIMS-UBM) technique

G. Kamath, A. P. Ehiasarian, Y. Purandare, P. Eh. Hovsepien

Nanotechnology Centre for PVD Research, Sheffield Hallam University, Sheffield, S1 1WB, United Kingdom

## ***Abstract:***

About 2.6 $\mu$ m thick TiAlCN/VCN Nanostructured multilayer with periodicity 2.3nm has been deposited by HIPIMS/HIPIMS+UBM technique, where HIPIMS is used for both surface pre-treatment as well deposition. The coatings were produced in industrial sized Hauzer HTC 1000-4 system enabled with HIPIMS technology by sputtering from 2-Vandium and 2-TiAl targets in a mixed CH<sub>4</sub>+Ar+N<sub>2</sub> atmosphere. The HIPIMS plasma composition was studied by Plasma sampling energy resolved mass spectrometer as a function of discharge current. Spectral intensities have shown high metal ion concentration of Ti<sup>+</sup>, V<sup>+</sup>, and Al<sup>+</sup> in the discharge. Significant amount of C<sup>+</sup> was also observed due to the decomposition of the reactive gas (CH<sub>4</sub>) as well as Ar<sup>+</sup> and N<sup>+</sup>. As a result highly dense microstructure of the multilayer has been achieved. This has been confirmed through the Cross-sectional TEM analyses. Thermo gravimetric analysis has shown a significant raise of oxidation resistant temperature  $\approx$  780°C, in contrast to carbon free TiAlN/VN multilayer coating. High temperature sliding wear test has been conducted on the coatings where friction coefficient was found to be decreasing from  $\mu=0.6$  to  $\mu=0.4$  when the temperature was increased from room to 650°C. XRD and Raman spectra taken on the wear track of coating has marked the presence of Magnelie phase oxides of the form, V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub>, TiO<sub>2</sub>, AlVO<sub>4</sub>.

## ***1. Introduction:***

One of the overarching challenges in current PVD technology is to provide nanostructured multilayer coatings suitable for machining of softer but “sticky” materials such as Ni-, Ti- and Al-based alloys. These coatings necessitate denser and smoother surface morphology, enhanced thermal and chemical stability and inertness relative to the work piece at elevated temperatures. Previously reported nanolaminate multilayer structures of TiAlN/VN deposited by standard Unbalanced Magnetron Sputtering (UBM) have shown promising performance

due to their very high hardness (>40 GPa), and low coefficient of friction defined by the formation of highly lubricious  $V_2O_5$  during dry sliding [1, ]. However, the problem with BUE formation during the dry sliding in high speed machining still remains.

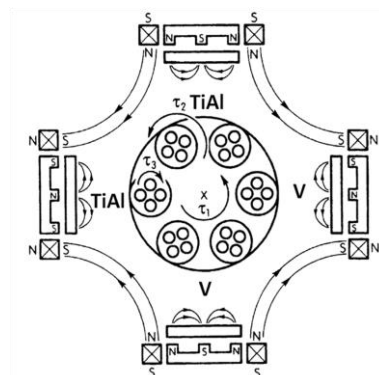
Recently TiAlCN/VCN and CrAlCN/CrCN nanostructured multilayer coatings were produced as an alternative to carbon-free TiAlN/VN multilayer structures [2, 3]. It was found that if carbon is added to the coating constitution to form TiAlCN/VCN and CrAlCN/CrCN, the micro-structure changes to a multilayer with unique architecture, where a carbon based phase is observed to exist between the individual layers of the nanolaminate. This phase is formed due to carbon segregation in the coating growth direction. The accumulation of carbon at the interfaces reduces their shear strength thus promoting nanolayer by nanolayer wear mechanism in sliding, which proved to be the key to elimination of BUE formation [3].

It is well understood that a competitive coating performance requires proper material, structure and deposition technology selection. High Power Impulse Magnetron Sputtering (HIPIMS) is an emerging technology which provides new alternative in the fabrication of nanoscale multilayer structures [4]. The unique aspect of the HIPIMS discharge is the production of highly ionised plasma containing almost equal concentration of gas and metal ions with higher energy states [5].

Previous research has confirmed unambiguously that when HIPIMS plasma is used for surface pre-treatment, enhanced adhesion can be achieved due to the production of atomically clean interface, preserved crystallinity of the substrate material and the promotion of local epitaxial growth of the coating over large areas [6]. It has also been shown that, during the deposition, the higher metal-to-gas ion ratio, higher dissociation rate of reactive gas, higher metal ionisation degree and higher energy of the condensing species attained in HIPIMS produces denser coatings by eliminating columnar voids formed due to atomic shadowing effect often observed in lower ion bombardment energy processes such as UBM for example [4,7]. The aim of this work is to show the effect of HIPIMS when employed in both surface pretreatment and coating deposition steps on the microstructure, oxidation resistance and thermal stability at elevated temperature of TiAlCN/VCN nanostructured multilayer coating.

## ***2. Deposition technique by HIPIMS/(HIPIMS-UBM) method:***

The deposition of TiAlCN/VCN nanoscale multilayer coating was carried out in an industrial sized PVD coating machine (HTC 1000-4 target system manufactured by Huzer Techno Coating, The Netherlands) enabled with HIPIMS technology at Sheffield Hallam University. The coating machine with chamber volume of 1 m<sup>3</sup> comprises four rectangular cathodes furnished with 2-TiAl (50:50 at% pure) and 2-V (99.8% pure) targets. The arrangement is shown schematically in Figure 1.



*Figure 1. Schematic cross-sectional internal view of Huzer HTC 1000-4*

The substrate was pretreated by bombardment of the surface with highly ionised  $V^+ + Ar^+$  plasma generated from a HIPIMS discharge sustained on the V target in Ar atmosphere. Details of this procedure are given in [8]. In the next step of the process, a 350 nm thick TiAlN base layer was deposited in Ar+N<sub>2</sub> atmosphere by operating one TiAl target in HIPIMS and one TiAl target in UBM mode. In the final stage of the coating, methane (CH<sub>4</sub>) gas was introduced in the vacuum chamber and deposition was carried out in a mixed Ar+N<sub>2</sub>+CH<sub>4</sub> reactive atmosphere at 450°C. In this stage, a pair of TiAl and V targets mounted opposite to each other was operated in HIPIMS mode whilst a second pair of targets from the same materials was operated in UBM sputtering mode to deposit 2.7µm thick TiAlCN/VCN coating. Effectively the base layer and the main coating were deposited in mixed HIPIMS-UBM mode, which has significantly compensated for the lower deposition rates available from pure HIPIMS sources without losing the effects of the ion assisted coating growth.

Throughout the process, the substrates were subjected to three-fold rotation. The substrate bias voltage during the coating deposition step was maintained at  $U_b = -75$  V. To maintain constant bias voltage in both surface pretreatment and coating deposition processes a specialised HIPIMS compatible bias power supply model HBP (Hüttinger Electronic Sp. z o.o.) was used [9].

The coatings were deposited on 30 mm diameter, 6 mm thick coupons from hardened M2 high-speed steel (HRC 62) and 25x25x0.2 mm, bright annealed 304

stainless steel coupons. All samples were mirror polished using 1  $\mu\text{m}$  diamond paste. Prior to the coating deposition the samples were cleaned in an automated cleaning line comprising a series of alkali solutions and de-ionized water baths followed by a vacuum drying furnace.

### ***3. Characterization techniques:***

A number of surface analysis techniques were employed to characterise the mechanical, tribological, and high temperature oxidation resistance.

The micro hardness of the coating was measured by an MVK-H2 Mitutoyo Knoop hardness tester, with normal load of 0.25 N. A CSM REVETEST scratch test analyser was used to determine the critical load,  $L_c$  (N) where first spallation of the coating takes place to characterise the adhesion strength of the coating. Cross-sections from as-deposited coatings were prepared for transmission electron microscopy (TEM) observation using Philips CM430 instrument.

A plasma sampling energy-resolved mass spectrometer PSM003 (Hiden Analytical Ltd.) was utilised to quantify the time-averaged ion composition in the plasma. The relative content of each ion was determined by integrating its corresponding ion energy distribution function. The plasma analysis has been carried out in a laboratory scale ultra- high vacuum chamber model CMS-18 (Kurt J. Lesker) equipped with 3-inch diameter targets of TiAl and V operated in HIPIMS and UBM discharge mode. The discharge conditions such as average and peak power density and gas pressure were similar to those of the deposition experiments conducted in the industrial sized Hauzer HTC-1000-4 machine.

To determine the oxidation resistance, thermo gravimetric analysis was carried out in high performance modular Thermo Gravimetric Analyser (TGA- ambient 1750°C) from SETARAM instrumentation. The micro-balance with a maximum load of 35 g, temperature drift stability of 5  $\mu\text{g}/^\circ\text{C}$  and mass sensitivity of 1  $\mu\text{g}$ . The TG samples (stainless steel 304 coupons with dimension 50 x 15 x 0.5 mm) were coated from all sides in order to eliminate substrate contributions during the oxidation process. Oxidation of TiAlCN/VCN multilayer coatings deposited by HIPIMS-UBM was assessed by TGA in the range from room temperature to 1000°C at a linear ramp rate of 1  $^\circ\text{C}/\text{min}$ .

A CSM pin-on-disc contact geometry room- and high temperature tribometers have been used to measure the friction and wear coefficient of the coated sample. 6 mm diameter  $\text{Al}_2\text{O}_3$  balls were used as counterparts under constant normal load of 5 N. Tests were carried out at circular speed of 10  $\text{ms}^{-1}$ , with wear track diameter of 7 mm at constant acquisition frequency of 1 Hz. The tests were conducted for 10 000 laps at room temperature and for 5000 laps at three different elevated temperatures, (200°C, 450°C, and 650°C) in ambient atmospheric condition. A precise wear track depth profiling was carried out using a Dektak 150 instrument to generate data for calculation of the coating sliding wear coefficient.

## 4. Result and discussion

### 4.1 Plasma compositional analysis:

The gas and metal ion compositions produced during the deposition process were determined separately for V metal ion etching (using V target in HIPIMS mode in Ar atmosphere) and coating deposition of TiAlCN and VCN (using TiAl and V targets in HIPIMS and UBM mode in Ar+N<sub>2</sub>+CH<sub>4</sub> atmosphere). Tables 1 and 2 show the percentage values of gas ions and individual metal ions (V, Ti, Al, and C) produced during the etching and coating deposition steps in HIPIMS and HIPIMS-UBM modes.

The results of the etching step (Table 1) clearly show the higher concentration of the detected ionisation states of V (V<sup>1+</sup>, V<sup>2+</sup>, V<sup>3+</sup>, V<sup>4+</sup> and V<sup>5+</sup>), which govern the surface etching and implantation processes. The high charge states are implanted deeper into the substrate ensuring a thicker and stronger diffusion layer. The high metal-to-gas ion ratio of 1.25:1 indicates that the surface is predominantly bombarded by metal ions, which is of great importance for preservation of the crystallinity of the coating-substrate interface and promotion of local epitaxial growth on such surfaces [6].

Table 2 summarises the plasma composition results acquired in the deposition step of the TiAlCN and VCN layers produced by HIPIMS and UBM techniques respectively. During TiAlCN deposition in HIPIMS mode, the metal ion content in the plasma was about 12% with Al<sup>1+</sup>=9%, Ti<sup>1+</sup>=2%, and C<sup>1+</sup>=1%. In UBM mode, detected metal ion content was factor 4 lower with ~3% distributed among Al<sup>1+</sup>= 2.8%, Ti<sup>1+</sup>= 0.23%, and C<sup>1+</sup>=0.13%.

Similarly, in VCN deposition, the metal ion concentration was found to be 7.73% in case of HIPIMS and significantly lower at 0.56% in case of UBM discharge. Free C<sup>1+</sup> ions were found at 8 times higher concentration in HIPIMS than UBM. The gas ion concentration was found to be about 91.78% and 99.26% for the HIPIMS and UBM discharge respectively.

The comparative results for TiAlCN and VCN are clearly showing the high metal-to-gas ion ratio of about 1:7 and 1:12 in HIPIMS discharge mode versus 1:32 and 1:177 in UBM discharge mode. The enhanced metal ion bombardment during HIPIMS deposition is expected to result in a denser microstructure with reduced intercolumnar porosity. Furthermore it can promote 2D layer-by-layer growth and reduce the roughness of the coatings.

*Table 1. Relative concentration of gas and V-metal ions produced during the HIPIMS pretreatment step of TiAlCN/VCN multilayer coating process.*

Process	Gas ions (%)			V-Metal ions (%)				
	Ar(1+)	Ar(2+)	Ar(3+)	V(1+)	V(2+)	V(3+)	V(4+)	V(5+)

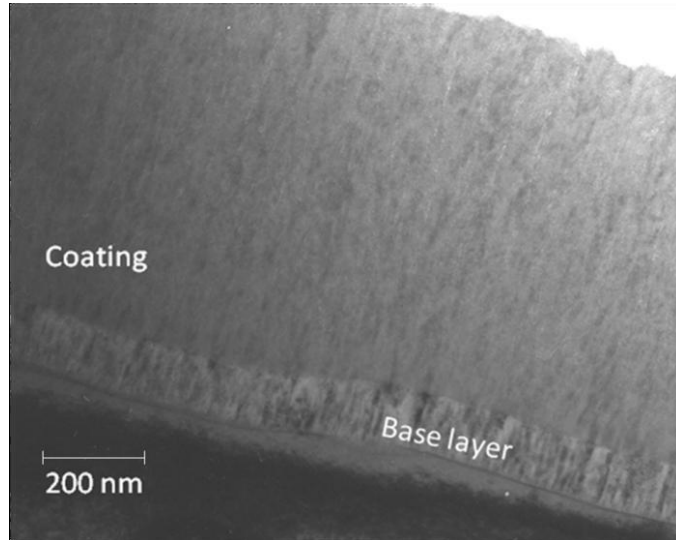
Pretreatment HIPIMS	31	12	1	24	27	4	0.8	0.2
------------------------	----	----	---	----	----	---	-----	-----

Table 2. Relative concentration of gas and metal ions of Ti,Al,V and C produced during the deposition of TiAlCN and VCN coating in HIPIMS and UBM mode. Gas ions include stable hydrocarbons ( $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$ ), radicals ( $CH$ ,  $CH_2$ ,  $CH_3$ ,  $C_2H$ ,  $C_2H_5$ ,  $C_3H_2$ ,  $C_3H_3$ ,  $C_3H_6$ ,  $C_3H_7$ ), and nitril compounds ( $HCN$ ,  $H_2CN$ ,  $NH$ , and  $NH_3$ )

Coating Deposition Process		Mode of deposition	
		HIPIMS	UBM
TiAlCN	Gas ions (%)	88	97
	Al(1+) (%)	9	2.6
	Ti(1+) (%)	2	0.25
	C(1+) (%)	1	0.13
VCN	Gas ions (%)	92	99
	V(1+) (%)	7.7	0.5
	C(1+) (%)	0.6	0.18

#### 4.2 Microstructural Investigation of as deposited TiAlCN/VCN multilayers by HIPIMS/(HIPIMS-UBM) technique.

Figure 2 shows a low magnification bright field TEM cross-section image of TiAlCN/VCN multilayer. The image clearly reveals that the utilization of HIPIMS during the deposition of the base-layer as well as the coating, results in a growth of extremely dense and smooth coating. This can be attributed to the high energy of the arrival particles resulting in high ad-atom mobility. The coating-substrate interface appears very sharp without any contamination or amorphous zone. This is attributed to the effective bombardment of the surface by high energy  $V^+$  metal ions generated in the HIPIMS discharge. Careful observation of the coating microstructure reveals a dense, free of inter-columnar voids coating, which is an indication for better protection against rapid oxidation at high temperatures and enhanced mechanical and tribological properties at elevated temperature.



*Figure 2. Cross-sectional BF-TEM image, showing the interface area and the highly dense columnar micro structure of TiAlCN/VCN deposited by HIPIMS-UBM*

#### **4.3 Thermo-Gravimetric (TG) analysis of the oxidation behaviour of TiAlCN/VCN**

TiAlN is probably one of the oldest PVD coatings dedicated to high temperature applications. Alloying TiN with Al was a successful approach due to formation of a double layer oxide scale ( $\text{TiO}_2/\text{Al}_2\text{O}_3$ ) where the dense top  $\text{Al}_2\text{O}_3$  layer provides a barrier for the diffusion of oxygen from the environment thus enhancing the oxidation resistance of the coating [10]. Reported values for the temperature of the onset of rapid oxidation of TiAlN are in the range of  $850^\circ\text{C}$  [11]. Unlike Al, addition of V and C to the coating constitution is expected to deteriorate the oxidation resistance; therefore the application of TiAlCN/VCN is restricted to the medium temperature range of up to  $800^\circ\text{C}$ .

Figure 3 shows the rate of oxide weight gain as a function of the temperature. The experiment reveals that the oxidation process develops in two stages. The initial slow mass gain at  $550^\circ\text{C}$  is believed to be due to oxidation of V which is then followed by a steep mass increase at  $800^\circ\text{C}$  representing the temperature for the onset of rapid oxidation of the entire coating. This value for



the onset of rapid oxidation however, is significantly higher than the earlier reported in the literature value ( $\approx 638^\circ\text{C}$ ) for the TiAlN/VN multilayer coating deposited by UBM technique [12]. The improved performance is believed to be due to the defect free closed columnar micro-structure achieved by more energetic ion bombardment during HIPIMS deposition process which in turn enhanced the oxidation resistance of the coating at elevated temperatures.

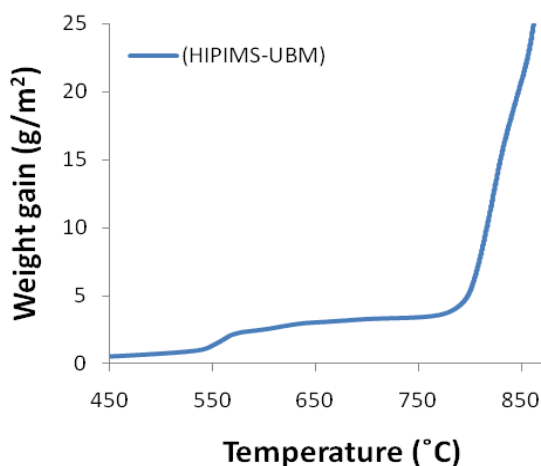
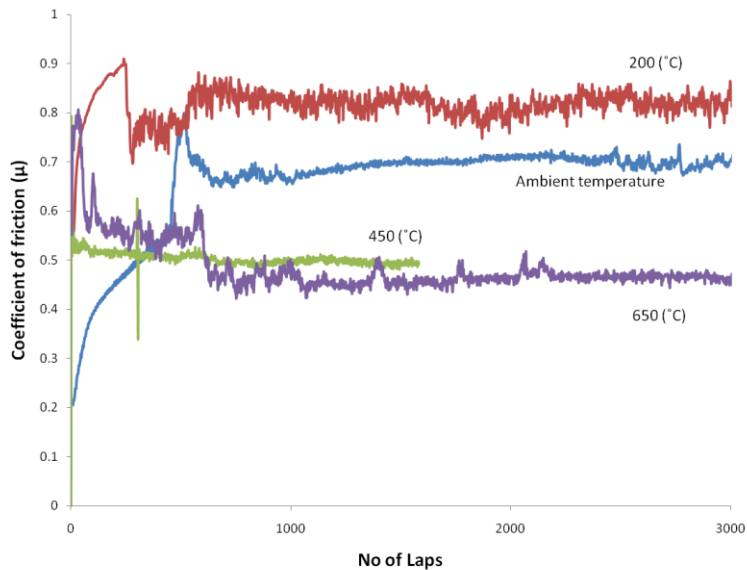


Figure 3. Thermo-Gravimetric (TG) curve of TiAlCN/VCN, showing the rate of oxide weight gain as a function of the temperature.

#### 4.4 Friction and wear analysis:

Figure 4 shows the coefficient of friction ( $\mu$ ) vs number of laps curve for TiAlCN/VCN coating during sliding for room and elevated temperatures of  $200^\circ\text{C}$ ,  $450^\circ\text{C}$ , and  $650^\circ\text{C}$ . Low friction coefficient of  $\mu=0.64$  and exceptionally low wear coefficient of  $1.4 \times 10^{-17} \text{ m}^3\text{N}^{-1}\text{m}^{-1}$  were measured for room temperature, which was attributed to the formation of the lubricious Magneli phase of  $\text{V}_2\text{O}_5$ . In general the lubricious effect of the Magneli phases such as  $\text{Ti}_n\text{O}_{2n-1}$ ,  $\text{V}_n\text{O}_{2n-1}$ ,  $\text{V}_n\text{O}_{3n-1}$  or  $\text{V}_n\text{O}_{3n-2}$  is explained by the presence of easy shearable crystallographic (CS) planes [13, 14]. Increase of the test temperature to  $200^\circ\text{C}$  resulted in increase of the coefficient of friction to  $\mu=0.8$  as well as increase of the wear coefficient to

$8.84 \times 10^{-14} \text{ m}^3 \text{N}^{-1} \text{m}^{-1}$ . Subsequently at  $450^\circ\text{C}$  and  $650^\circ\text{C}$ , a gradual decrease in the friction coefficient value to  $\mu=0.5$  and  $\mu=0.45$  was observed whereas the wear rate was negligibly increased to  $9 \times 10^{-14}$  -to-  $11 \times 10^{-14} \text{ m}^3 \text{N}^{-1} \text{m}^{-1}$  respectively. The initial increase of the coefficient of friction can be attributed to the removal of the condensed water vapour film from the sliding surface which has lubricious effect. Further increase of the temperature however leads to intensive surface oxidation produced by the combined action of the high temperature exposure to air as well as the sliding wear. XRD analyses reported previously for TiAlN/VN coatings show formation of a range of oxides such as  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  mixed with  $\text{AlVO}_4$  all possessing lubricious properties due to their crystallographic structure [12,15]. Additionally in the case of the TiAlCN/VCN multilayer coatings the presence of a carbon based phase between the individual layers of the nanolaminate further influences the wear behaviour by introducing layer by layer wear mechanism as reported previously [ 3].



*Figure 4. Coefficient of friction curves for TiAlCN/VCN coating during sliding for room and elevated temperatures of  $200^\circ\text{C}$ ,  $450^\circ\text{C}$ , and  $650^\circ\text{C}$ .*

#### **4.5 Raman analysis:**

Raman spectroscopy has proven to be a powerful tool to study worn surfaces and define the phase composition of the wear products [16]. Figure 5 shows Raman spectra undertaken on the as-formed wear debris accumulated along the side of the wear track in the pin-on-disk test carried out at various temperatures, (ambient, 200, 450 and 650°C).

At ambient and 200°C temperatures a series of broad Raman bands centred at 237, 652, 896, 1321 and 1579  $\text{cm}^{-1}$  were observed, Figure 5. The spectra in the 200  $\text{cm}^{-1}$  to 800  $\text{cm}^{-1}$  band looks similar to the spectrum of TiAlN [17] except for the presence of  $\text{V}_2\text{O}_5$  in the 600-800  $\text{cm}^{-1}$  band [16]. The subsequent broad peak in-between 800- to-1000  $\text{cm}^{-1}$  can be assigned to the presence of highly crystalline  $\alpha\text{-Al}_2\text{O}_3$  [16] or  $\text{AlVO}_4$  phase which could be resulted due to reaction between the wear product from the alumina counterpart ( $\text{Al}_2\text{O}_3$  ball) and  $\text{V}_2\text{O}_5$  [18]. The highly diffused peaks corresponding to the disordered and graphitic carbon band were also detected in the 1200-1600  $\text{cm}^{-1}$  band. These observations lead to the conclusion that at low temperatures up to 200°C the wear product contains debris of the as deposited coating as well as V based oxides formed due to high flash temperatures at the asperity contacts during sliding. This is in good agreement with the TG experiments where first effect of oxidation is observed at 550°C.

At 450°C the oxide formation is influenced not only by tribo-oxidation but also due to the external heating of the sample. The peaks of the spectra are with higher intensity and depict the presence of  $\text{V}_2\text{O}_5$  phase in the 200-to-600  $\text{cm}^{-1}$  band and  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{AlVO}_4$  in the 600 to 1000  $\text{cm}^{-1}$  band. It is also important to notice that the amorphous carbon D and G bands in between 1321  $\text{cm}^{-1}$  and 1579  $\text{cm}^{-1}$  have shown more intensity, which suggests graphitization process taking place during sliding.

At 650°C the peaks in the 200-700  $\text{cm}^{-1}$  band appear with higher intensity showing formation of a mixture of several oxides such as  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{TiO}_2$ . This spectral range have also shown significant amount of V-containing Aluminium oxide phase, most probably  $\text{AlVO}_4$  as identified by XRD analyses. The  $\alpha\text{-Fe}_2\text{O}_3$  is contributed by wear debris of the substrate material. More interestingly a graphitic peak was identified in between 1300-1400  $\text{cm}^{-1}$  corresponding to the D band of disordered graphite. This suggests that the carbon phase has a clear contribution to the friction and wear behaviour of TiAlCN/VCN at elevated temperatures.

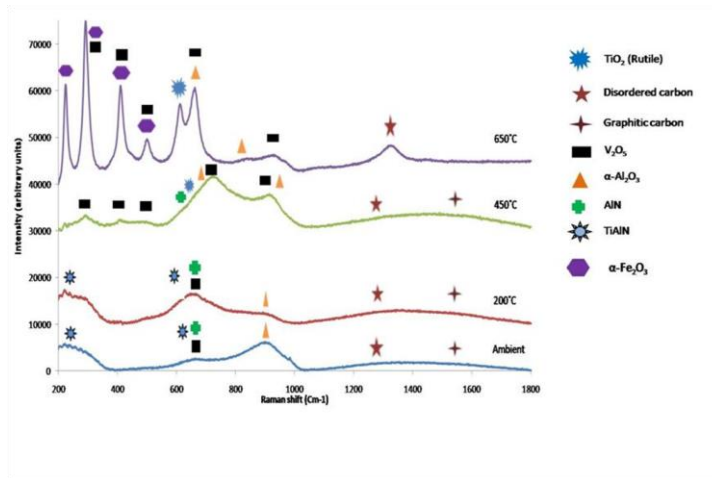


Figure 5. Raman spectra of the wear debris generated at ambient, 200°, 450° and 650°C in the wear track during pin-on-disk test.

In summary, the Raman studies have identified the generation of highly lubricious phases such as ( $V_2O_5$ ,  $TiO_2$ ,  $AlVO_4$ ) during sliding at room and elevated temperature thus providing additional tool for better understanding the high temperature tribological behaviour of TiAlCN/VCN.

## 5. Conclusions:

- The time averaged mass spectrometry results have confirmed the presence of higher concentration of metal ions with higher energy states (up to +5) of the HIPIMS of V plasma during the surface pre-treatment stage. The subsequent comparative mass spectrometry analysis carried out during the HIPIMS deposition of TiAlCN and VCN have shown higher concentration of metal ions in contrast to UBM deposition mode. Hence, high metal ion bombardment has been achieved during the HIPIMS involved etching and deposition step of TiAlCN/VCN multilayer. Consequently, the HIPIMS has promoted the layer-by-layer growth during the deposition thus resulting in void free denser micro-structure with reduced roughness.
- The Thermo-gravimetric analysis has shown the increased oxidation resistance ( $\approx 800^\circ C$ ) of the coating which can be attributed to the defect free closed columnar micro-structure achieved by high energy metal ion irradiation.

- The Pin-On-disc measurement has resulted in significant reduction in the friction coefficient from 0.67 at ambient temperature to about  $\approx 0.5$  at 450 °C and  $\approx 0.4$  at 650 °C following the layer-by-layer wear mechanism.
- The Raman analysis of as-formed wear debris during the dry sliding process have identified the generation of highly lubricious phases such as ( $V_2O_5$ ,  $TiO_2$ ,  $AlVO_4$ ) during the sliding at room and elevated temperatures. Effectively, the void free denser microstructure of TiAlCN/VCN multilayer coating achieved by utilizing HIPIMS has shown enhanced oxidation and tribological behaviour at elevated temperature.

#### References:

- [1] P. Eh. Hovsepian, Q.Luo, G. Robinson, M. Pittsman, M. Howarth, D. Doerwald, R. Tietema, W.-M. Sim, A. Deeming, T. Zeus, TiAlN/VN superlattice structured PVD coatings: A new alternative in machining of aluminium allows for aerospace and automotive components, *Surf, Coat Technol* 201(2006) 265-272.
- [2] P. Eh. Hovsepian, A.P. Ehiasarian, A. Deeming, C. Schimpf. Novel TiAlCN/VCN Nanoscale Multilayer PVD Coatings Deposited by the Combined High Power Impulse Magnetron Sputtering / Unbalanced Magnetron Sputtering, (HIPIMS/UBM) Technology, *Vacuum* 82 (2008) 1312-1317.
- [3] P. Eh. Hovsepian, A.P. Ehiasarian, I. Petrov, C. Schimpf. TiAlCN/VCN Nanoscale Multilayer PVD Coatings Deposited by the Combined High Power Impulse Magnetron Sputtering/ Unbalanced Magnetron Sputtering, (HIPIMS/UBM) Technology Dedicated to Machining of Al and Ti Alloys. *Surface Engineering*. DOI 10.1179/026708408X336337.
- [4] P. Eh. Hovsepian, A. P. Ehiassarian, Y. P. Purandare, R. Braun, I.M. Ross, Effect of high ion irradiation on the structure, properties and high temperature tribology of nanoscale CrAlYN/CrN multilayer coating deposited by HIPIMS-HIPIMS technique, *Plasma Processes and Polymers*, Vol. 6, issue S1, 2009, pp. S118 – S123.
- [5] A.P. Ehiasarian, R. New, W.-D. Münz, I. Hultman, U. Helmersson, V. Kouznetsov, Influence of high power densities on the composition of pulsed magnetron plasmas, *Vacuum*, 2002, 65, 147

- [6] A.P. Ehiasarian, J.G. Wen, I. Petrov, Interface microstructure engineering by high power impulse magnetron sputtering for the enhancement of adhesion, , Journal of Appl. Physics 101 (2007), 054301.
- [7] Y. P. Purandare, A. P. Ehiasarian, and P. Eh. Hovsepien. Deposition of Nanoscale Multilayer CrN/NbN Physical Vapour Deposition Coatings by High Power Impulse Magnetron Sputtering. *J. Vac. Sci. Technol. A* 26, 2, Mar/Apr 2008, p288-296.
- [8] A. P. Ehiasarian, P. Eh. Hovsepien, W.-D.Münz, , “A Combined Process Comprising Magnetic Field-Assisted, High-Power, Pulsed Cathode Sputtering and an Unbalanced Magnetron”: US Pat. 7081186B2, 2005, EP 1 260 603 A2, DE 10124749, 21.05. 2001.
- [9] A. P. Ehiasarian, P. Eh. Hovsepien, R. Tietema, R. Bugyi, "A vacuum treatment apparatus, a bias power supply and a method of operating a vacuum treatment apparatus", H10107GB, 11 April 2006.
- [10] D.McIntyre, J.E.Greenne, G. Håkansson, J.-E.Sundgren and W.-D. Münz, (1990). Oxidation of metastable single-phase polycrystalline  $Ti_{0.5}Al_{0.5}N$  films: Kinetics and mechanisms. *J. Appl. Phys.* 67: 1542-1553.
- [11] W.-D Münz, Titanium aluminium nitride films – a new alternative to TiN coatings. *J. Vac. Sci. Technol.* (1986) A4(6): 2717-2725.
- [12] Z. Zhou, W.M. Rainforth, D.B. Lewis, S. Creasy, J.J. Forsyth, Clegg E, A.P Ehiasarian, P.Eh Hovespien, W-.D. Munz., Oxidation behaviour of nanoscale TiAlN/VN multilayer coatings, *Surface and Coatings Technology*, 177: (2004)198-203.
- [13] M.N.Gardos, Magnéli phases of anion-deficient rutile as lubricious oxides. Part I. Tribological behavior of single-crystal and polycrystalline rutile ( $Ti_nO_{2n-1}$ ), *Tribology letters* 8 (2000) 65-78.
- [14] M. Woydt, A. Skopp, I. Dorfel, K. Witke, Wear engineering oxides/anti-wear oxides, *Wear* 218 (1998) 84–95.
- [15] D. B. Lewis, S. J. Creasey, Z. Zhuo ,J.J. Forsyth, A. P. Ehiasarian P. Eh. Hovsepien, Q. Loo, W. M. Rainforth , W.-D. Münz , The effect of (Ti+Al):V ratio on the structure and oxidation behaviour of TiAlN/VN nano-scale multilayer coatings. *Surf, Coat and Technol* 177-178 (2004), p. 252-259.
- [16] C.P. Constable, J. Yarwood, P. Hovsepien, L.A. Donohue, D.B. Lewis, W.-D. Münz, Structural determination of wear debris generated from sliding wear

tests on ceramic coatings using Raman microscopy. *J. Vac. Sci. Technol. A* 18(4), Jul/Aug (2000), p. 1681.

[17] H. C. Barshilia, K.S.Rajam, A Raman-scattering study on the interface structure of nanolayered TiAlN/TiN and TiN/NbN multilayer thin films grown by reactive dc magnetron sputtering, *J. Appl. Phy.* 98 (2005)

[18] N. Fateh, G.A. Fontalvo, G. Gassner, C. Mitterer, Influence of high-temperature oxide formation on the tribological behaviour of TiN and VN coatings. *Wear* 262, (2007), 1152-1158.