Lubricious TiSi(V)N coatings for extreme temperature application deposited by Deep Oscillation Magnetron Sputtering (DOMS) mode

F. Fernandes[1*], M.A. Mekicha[1], J.C. Oliverira[1], T. Polcar[2, 3], A. Cavaleiro[1]
[1]SEG-CEMUC - Department of Mechanical Engineering, University of Coimbra, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal.
[2]National Centre for Advanced Tribology (nCATS), School of Engineering Sciences, University of Southampton, Highfield, Southampton, SO17 1BJ, UK.
[3]Department of Control Engineering Czech Technical University in Prague Technicka 2, Prague 6, 166 27 Czech Republic.
*e-mail: filipe.fernandes@dem.uc.pt

ABSTRACT

Development of new self-lubricant coating systems with control of the lubricous species diffusion have enormous potential to be used in the protection of surfaces in components for machining. In the last years, vanadium rich coatings have been introduced as possible candidates for self-lubrication due to their optimum tribological properties. This work is devoted on the study of V additions on the morphology, structure and on the tribological properties of TiSiN films deposited by HiPIMS in Deep Oscillation Magnetron Sputtering (DOMS) mode. Two different peak powers were used on the deposition of coatings in order to produce films with different morphology. The tribological properties of coatings were evaluated at room temperature against Al_2O_3 balls on a pin-on-disc apparatus. Increasing of peak power showed to change the cross section morphology of films from columnar type to compact structure. V additions improved the tribological properties of TiSiN coatings.

KEY WORDS: Lubricious TiSi(V)N films, DOMS, Tribology

1. INTRODUCTION

Dictated by elimination of coolant media utilisation and environmental protection requirements, recently milling and cutting operations are making a transition to dry machining. This shift in machining technology requires machining tools to withstand harsh working conditions combining oxidation, abrasion, adhesion, thermal and mechanical loads. Solid lubricant coatings such as diamond like carbons (DLCs), transition metal dichalcogenides (TMD), and WC/C have been used in improving performance and lifetime of the cutting tools. However, their tribological properties degrade in humid atmospheres and/or at elevated temperatures due to their low oxidation resistance. To overcome this shortcoming, a new concept of high temperature lubrication has been proposed. Solid lubricant coatings have been developed by combining the intrinsic properties of some binary or ternary films (TiN, CrN, CrAlN, TiAlN, YSZ, etc), which are very hard and resistant to oxidation, with specific elements (metals), which diffuse to the surface and form a low friction tribolayer (as a metal layer, e.g. Ag, Cu, Au, Pb and In, or a low-friction oxide, e.g. V_2O_5, $Ag_2Mo_2O_7$) [1-4]. Among these elements, particular attention has been given to the vanadium-containing coatings (Magnéli phases V_nO_{2n-1}), which showed interesting tribological properties in the temperature range 500–700 ºC [5-11].

Dissimilar series of V-based hard coatings have been developed, such as ternary CrVN [12], (V,Ti)N [13], multilayer AlN/VN [14] and quaternary single layered or multilayered AlCrVN [15, 16] and TiAlVN [8, 17-19]. Independently of the configuration, the friction was decreased and the wear resistance improved.

However, such improvements were of short duration due to the rapid release of vanadium. The quick out diffusion of V from the coating results in the consequent loss of the low friction properties after few minutes [20]. The control of V out-diffusion is now one of the major challenges to achieve a suitable long lasting wear and friction properties without compromising the original properties of the host binary and ternary films. Therefore, one possible proposal to solve this problem is to use coating systems with a dual phase structure, such as the case of TiSiN system, in which one of the phases (Si_3N_4) could act as a diffusion barrier to the lubricious phase metal (V) release.

The purpose of this work is to study the effect of V addition on high temperature tribological properties of TiSi(V)N coatings deposited by high power impulse magnetron sputtering (HiPIMS) in deep oscillation mode (DOMS) as it has been reported to allow easily tailor the nanocomposite structure of the TiSiN films; condition necessary to produce films with proper barrier to the lubricious species to achieve long term lubrication [21]. TiSiN system was selected because of its very high oxidation resistance similar to TiAlN, and TiCrN but can be deposited with much better mechanical properties. Two series of coatings (using two different peak powers) were deposited with increasing V content, in order to evaluate the effect of V addition on the surface and cross section morphology, structure and tribological properties of TiSiN films.

2. EXPERIMENTAL PROCEDURE

Six TiSi(V)N films were deposited in reactive, unbalanced mode by DOMS (HiPIMS Cyprium™III plasma generator, Zpulser Inc.) at a deposition pressure of 1.2 Pa without bias. Prior to the depositions, all the substrates were ultrasonically cleaned in acetone and alcohol. The substrates were then mounted in a rotating (18 revs/min) substrate holder. A square (150 × 150 mm) of high purity Ti (99.9%) target with 20 holes (10 mm in diameter) uniformly distributed throughout the preferential erosion zone was used. The holes were filled with different number of pellets of high purity Si (99.9%) and high purity V (99.9%), in order to achieve a desired Si and V content, with the remaining holes filled with Ti pellets. A total of six depositions were made. All the coatings were deposited with 7% of Si using two different peak powers (28.31 kW and 109.83 kW), with increasing V content (0, 5, and 10 at.%, achieved by using 0, 5, and 9 pellets of V at the Ti target, respectively). Hereinafter the coatings will be designated as $TiSiN_y$, or $TiSiV_xN_y$ where y denotes the peak power and x the number of V pellets introduced at the Ti target. Thus, coatings with y = 1 and 2 means that the coatings were deposited with peak powers of 29.31 kW and 109.83 kW, respectively. Table 1 shows the sample designation adopted for coatings identification. Before making the deposition, the chamber was evacuated down to $5{\times}10^{-4}$ Pa. Ion gun plasma was used to clean the substrates before depositions. The films were deposited onto silicon wafers for structure analysis, cross section, surface morphology characterization and chemical composition evaluation; stainless steel discs (Ø 20 × 1 mm) for residual stress measurements and AISI M2 (Ø 24 x 7.9 mm) substrates for tribological characterization. The chemical composition of the coatings was evaluated by energy dispersive spectroscopy (EDS). TiSiN and TiSiVN films with different Si and V contents as measured by Electron Probe Microanalysis (EPMA), from previous depositions [22], were used as reference for the EDS measurements. The chemical composition of the films are plotted in Table 2. Scanning electron microscopy (SEM) was used to examine the thickness, fracture cross section and surface morphologies of films. The crystallographic structure was investigated by X-ray diffraction (X' Pert Pro MPD diffractometer) using a grazing incidence angle of 3^o and Cu Kα1 radiation (λ = 1.54060 A). The tribological behavior of films was evaluated on a pin-on-disc tribometer at room temperature, using 5N normal load, 5.3 mm wear track radius, 10 cm/s linear speed and 3000 cycles. Al_2O_3 ball of grade 20 with diameter 7.94 mm was used as a counterpart. The friction coefficient was continuously measured and the wear rate of films determined from the wear track using a Zygo – NewView 7200, 3D profilometer.

Table 1 - Sample designation of coatings.

Coating	Number of V pellets	Peak power (kW)	Designation
TiSiN	0	28.31	$TiSiN_1$
TiSiVN	5		$TiSiV_5N_1$
	9		$TiSiV_9N_1$
TiSiN	0	109.83	$TiSiN_2$
TiSiVN	5		$TiSiV_5N_2$
	9		$TiSiV_9N_2$

Table 2 - Chemical composition of the coatings in at.%.

Coating	at.%			
	N	Si	V	Ti
$TiSiN_1$	61.76	6.69		31.55
$TiSiV_5N_1$	60.42	6.73	5.29	27.56
$TiSiV_9N_1$	60.07	6.27	9.89	23.77
$TiSiN_2$	62.45	6.25		31.29
$TiSiV_5N_2$	60.81	6.94	4.79	27.45
$TiSiV_9N_2$	60.11	6.44	10.18	23.27

3. RESULTS AND DISCUSSION

3.1. Surface and cross section morphology of coatings

Figure 1 displays the effect of change of peak power and increasing V content on the surface and fracture cross section micrographs of TiSi(V)N coatings. Coatings deposited with the low peak power (Figures 1 a), b) and c)) showed a typical columnar structure, while, the ones deposited with the high peak power (Figs. 1 d), e) and f)) displayed a compact morphology, although some very small remains columns are still observed. The increasing of compactness level can be attributed to the increasing of the bombarding species energy with increasing peak power [21]. As V content was increased, in both TiSiN reference films, the columns size and the surface roughness were increased.

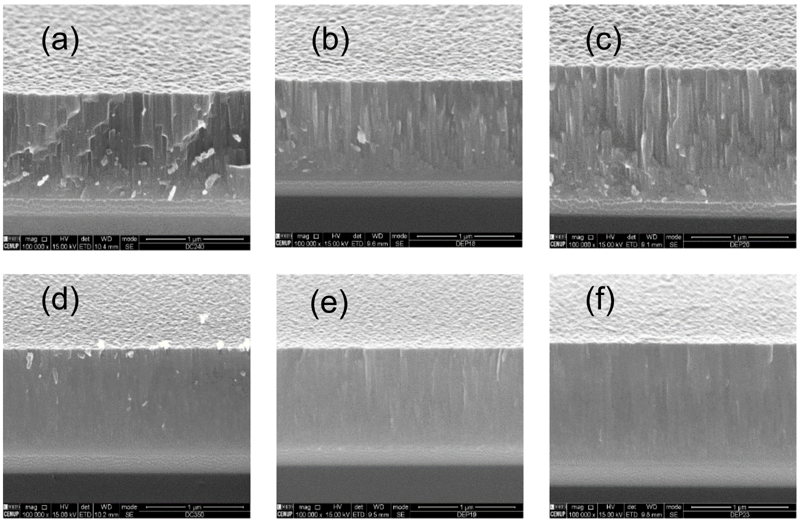

Figure 1 - Surface and cross section morphology of coatings deposited with low peak and high peak power. Low peak power: (a), (b), (c) $TiSiN_1$, $TiSiV_5N_1$, $TiSiV_9N_1$ respectively; and high peak power: (d), (e), (f) $TiSiN_2$, $TiSiV_5N_2$, $TiSiV_9N_2$, respectively.

3.2. Structure

The corresponding X-ray diffraction patterns of the as-deposited coatings are displayed in figure 2. The effect of the peak power on the structure of the coatings is shown in spectrums a) and b), whilst the effect of V additions in each of the previous TiSiN films is displayed in spectrums c-d and e-f for coatings deposited with low and high peak power, respectively. All the diffraction peaks could be generally assigned to the f.c.c NaCl type TiN phase. However, depending on the power supply used and on the V content on the films, different peak positions, intensities and broadening can be observed. Increasing the peak power on TiSiN films shift the diffraction peaks to lower angles. Such behavior can be attributed to the increase of compressive residual stresses on the film with increasing peak power. Compressive residual stresses of 1.96 and 2.99 GPa were calculated (based on the Stoney equation) for the TiSiN films deposited with low and high peak power, respectively. The increase of the level of compressive residual stresses with increasing peak power can be attributed to the increase of ions energy, as reported elsewhere [21]. With increasing V content, the fcc peaks are shifted to higher angles, behavior associated to a smaller unit cell. Since similar levels of compressive residual stresses were measure for each series of the V rich coatings in respect to the references TiSiN films, this behavior can only be explained by substitution of Ti by the smaller V atoms, which due to its smaller atomic radius promotes the contraction of the TiN lattice. Similar trend was observed by Pfeiler et al. [17] for the TiAlVN system and by Fernandes et al. [22] for TiSi(V)N system deposited by DC reactive magnetron sputtering.

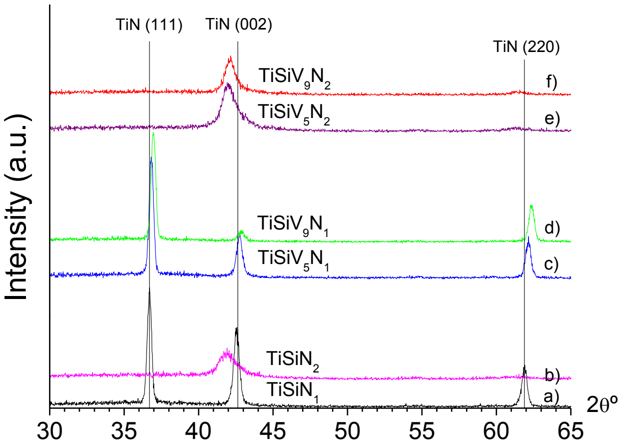

Figure 2 - X–ray diffraction patterns of TiSi(V)N films deposited with increasing peak power and with increasing V content. a) $TiSiN_1$, b) $TiSiN_2$, c) $TiSiV_5N_1$, d) $TiSiV_9N_1$, e) $TiSiV_5N_2$, f) $TiSiV_9N_2$.

3.3. Tribological behavior

Figure 3 shows the friction coefficient, specific wear rate and the 2D profiles of the wear track of the different coatings tested against Al_2O_3. TiSiN coating deposited with low peak power showed higher specific wear rate than coating produced with high peak power. This result agrees with the friction coefficient values and can be attributed to the high hardness of the $TiSiN_2$ film (31.55 against 22.9 GPa for $TiSiN_1$ film). In all cases, the addition of vanadium resulted in a reduction of the friction coefficient (see figure 3 (a)) and also on the improvement of the wear resistance. These improvements in tribological properties can be attributed to the formation of lubricious vanadium oxides on the wear track of coatings as revealed EDS and Raman analysis (not shown here).

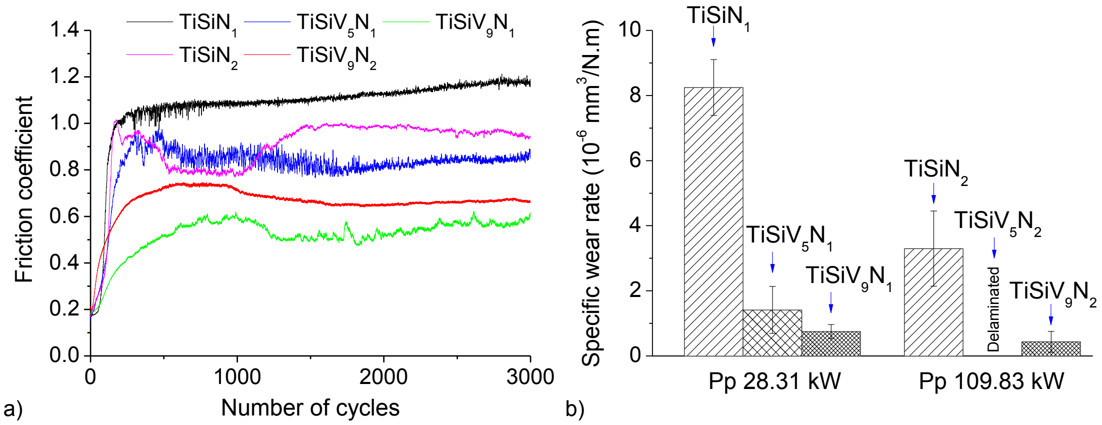

Figure 3 - (a) friction coefficient, (b) specific wear rate, and (c) 2D wear track profile of TiSi(V)N coatings.

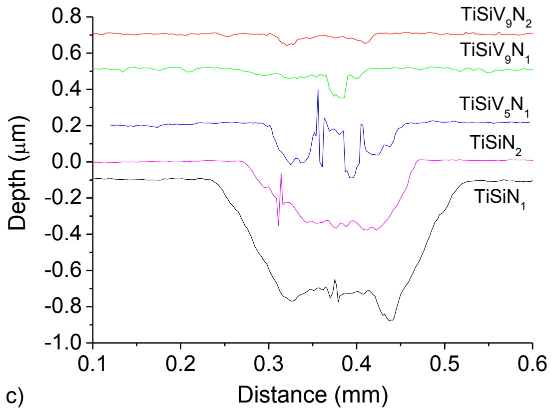

Figure 3 (continued)

4. CONCLUSION

The results showed that independently of the peak power used on the deposition and/or the v content present on the films, all the coatings displayed diffraction peaks assigned to crystalline f.c.c NaCl type TiN phase. The increase of peak power in TiSiN films showed to shift the diffraction peaks to lower angles, behavior attributed to the increasing of the bombarding species energy with increasing peak power, which increases the level of compressive residual stresses on the films. A shift of the diffraction peaks to higher angles is observed with increasing V content on the TiSiN films, suggesting the formation of a substitutional solid solution in TiN phase. This behavior showed to be independent of the peak power applied on the coatings although different changes in peaks intensity and broadening were noticed. V additions to TiSiN films decreased the wear rate and the friction coefficient of coatings, due to vanadium oxide formation.

ACKNOWLEDGEMENTS

This research is sponsored by FEDER funds through the program COMPETE – Programa Operacional Factores de Competitividade – and by national funds through FCT – Fundação para a Ciência e a Tecnologia, under the projects: PTDC/EME-TME/122116/2010 and PTDC/EMS-TEC/1805/2012. The authors acknowledge the Master student Melkamu A. Mekicha (co-author of this paper) from the International Joint European Master in Tribology of Surfaces and Interfaces (TRIBOS) program, doing his thesis in the mechanical engineering department of the University of Coimbra, for his special dedication on the development of this research.

REFERENCES

[1] S.M. Aouadi, H. Gao, A. Martini, T.W. Scharf, C. Muratore, Lubricious oxide coatings for extreme temperature applications: A review, Surf. Coat. Technol. 257 (2014) 266-277.
[2] R. Franz, C. Mitterer, Vanadium containing self-adaptive low-friction hard coatings for high-temperature applications: A review, Surf. Coat. Technol., 228 (2013) 1-13.
[3] T.W. Scharf, S.V. Prasad, Solid lubricants: a review, J. Mater. Sci., 48 (2013) 511-531.

[4] A.A. Voevodin, C. Muratore, S.M. Aouadi, Hard coatings with high temperature adaptive lubrication and contact thermal management: review, Surf. Coat. Technol. 257 (2014) 247-265.

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

[6] D.B. Lewis, S. Creasey, Z. Zhou, J.J. Forsyth, A.P. Ehiasarian, P.E. Hovsepian, Q. Luo, W.M. Rainforth, W.D. Münz, The effect of (Ti+Al):V ratio on the structure and oxidation behavior of TiAlN/VN nano-scale multilayer coatings, Surf. Coat. Technol., 177–178 (2004) 252-259.

[7] K. Kutschej, P.H. Mayrhofer, M. Kathrein, P. Polcik, C. Mitterer, A new low-friction concept for Ti1−xAlxN based coatings in high-temperature applications, Surf. Coat. Technol., 188–189 (2004) 358-363.

[8] K. Kutschej, P.H. Mayrhofer, M. Kathrein, P. Polcik, C. Mitterer, Influence of oxide phase formation on the tribological behavior of Ti–Al–V–N coatings, Surf. Coat. Technol., 200 (2005) 1731-1737.

[9] G. Gassner, P.H. Mayrhofer, K. Kutschej, C. Mitterer, M. Kathrein, A New Low Friction Concept for High Temperatures: Lubricious Oxide Formation on Sputtered VN Coatings, Tribology Letters, 17 (2004) 751-756.

[10] P.H. Mayrhofer, P.E. Hovsepian, C. Mitterer, W.D. Münz, Calorimetric evidence for frictional self-adaptation of TiAlN/VN superlattice coatings, Surf. Coat. Technol., 177–178 (2004) 341-347.

[11] A. Glaser, S. Surnev, F.P. Netzer, N. Fateh, G.A. Fontalvo, C. Mitterer, Oxidation of vanadium nitride and titanium nitride coatings, Surface Science, 601 (2007) 1153-1159.

[12] M. Uchida, N. Nihira, A. Mitsuo, K. Toyoda, K. Kubota, T. Aizawa, Friction and wear properties of CrAlN and CrVN films deposited by cathodic arc ion plating method, Surf. Coat. Technol., 177–178 (2004) 627-630.

[13] J.H. Ouyang, S. Sasaki, Tribo-oxidation of cathodic arc ion-plated (V,Ti)N coatings sliding against a steel ball under both unlubricated and boundary-lubricated conditions, Surf. Coat. Technol., 187 (2004) 343-357.

[14] J.-K. Park, Y.-J. Baik, Increase of hardness and oxidation resistance of VN coating by nanoscale multilayered structurization with AlN, Mater. Lett., 62 (2008) 2528-2530.

[15] R. Franz, J. Neidhardt, R. Kaindl, B. Sartory, R. Tessadri, M. Lechthaler, P. Polcik, C. Mitterer, Influence of phase transition on the tribological performance of arc-evaporated AlCrVN hard coatings, Surf. Coat. Technol., 203 (2009) 1101-1105.

[16] Y. Qiu, S. Zhang, J.-W. Lee, B. Li, Y. Wang, D. Zhao, Self-lubricating CrAlN/VN multilayer coatings at room temperature, Applied Surface Science, 279 (2013) 189-196.

[17] M. Pfeiler, K. Kutschej, M. Penoy, C. Michotte, C. Mitterer, M. Kathrein, The effect of increasing V content on structure, mechanical and tribological properties of arc evaporated Ti–Al–V–N coatings, International Journal of Refractory Metals and Hard Materials, 27 (2009) 502-506.

[18] W. Tillmann, S. Momeni, F. Hoffmann, A study of mechanical and tribological properties of self-lubricating TiAlVN coatings at elevated temperatures, Tribology International, 66 (2013) 324-329.

[19] Q. Luo, Temperature dependent friction and wear of magnetron sputtered coating TiAlN/VN, Wear, 271 (2011) 2058-2066.

[20] F. Fernandes, PhD Thesis: Surface Modification of Molds and Acessories for the Glass Industry, Developed at the Mechanical Engineering Department of the University of Coimbra, University of Coimbra, Coimbra, 2014, Portugal.
[21] J.C. Oliveira, F. Fernandes, F. Ferreira, A. Cavaleiro, Tailoring the nanostructure of Ti–Si–N thin films by HiPIMS in deep oscillation magnetron sputtering (DOMS) mode, Surf. Coat. Technol., 264 (2015) 140-149.
[22] F. Fernandes, A. Loureiro, T. Polcar, A. Cavaleiro, The effect of increasing V content on the structure, mechanical properties and oxidation resistance of Ti–Si–V–N films deposited by DC reactive magnetron sputtering, Applied Surface Science, 289 (2014) 114-123.