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Oxidation and diffusion processes during annealing of TiSi(V)N films

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Abstract

The degradation of self-lubricant hard coatings applied in tools for high-speed cutting or dry drilling operations occurs by a combination of wear, oxidation and diffusion. The aim of this investigation was to study the effect of V additions on the diffusion processes and on the oxide scale formation during annealing of TiSiVN coatings. Relation of these results with those achieved for a reference Ti₀.₈₀Si₀.₁₅N coating with similar Si content is also presented. The structure evolution of the Ti₀.₆₅Si₀.₁₁V₀.₁₅N film was assessed by an in-situ hot-XRD device. A dual layer oxide was formed in the case of Ti₀.₈₀Si₀.₁₅N coating with a protective Si-O layer at an oxide/coating interface;
however, in zones of film defects a complex oxide structure was developed. V additions increased the oxidation rate of the coatings as a result of the V ions diffusion throughout the oxide scale, which inhibited the formation of a continuous protective silicon oxide layer.

Keywords: TiSiVN system, structural evolution, oxidation, oxide scale, diffusion processes

1. Introduction

The reduction of the wear and friction coefficient of machining tools during in-service conditions remains an important challenge today in order to increase their lifetime and performance. Traditionally, oils and other liquid lubricants have been used to reduce the friction between the cutting tool and piece primarily by shearing the oil molecules across the solid-liquid-solid interface. However, most of the liquid lubricants volatilize at high temperature, which leads to the dry sliding and consequent failure of the cutting tools resulting in the increasing machine down times, higher process instability, poor product quality and higher costs [1]. To face these problems, a wide range of solid lubricant coatings, such as WC/C, MoS$_2$, diamond-like carbon (DLC), h-BN as well as their combinations in nanocrystalline or multilayer structures, have been developed in the last decades and successfully applied in order to improve the tribological behaviour under dry machining conditions [2-5]. However, considerable degradation of the tribological effectiveness of these coatings at elevated temperature has been reported due to their low resistance to oxidation. 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. $V_2O_5$, $Ag_2Mo_2O_7$) [6-9]. 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°C [2, 10-15]. Dissimilar series of V-based hard coatings have been developed, such as ternary CrVN [16], (V,Ti)N [17], multilayer AlN/VN [18] and quaternary single layered or multilayered AlCrVN [19, 20] and TiAlVN [12, 21-23]. Independently of the configuration, the friction was decreased and the wear resistance improved; however, the oxidation resistance was degraded. For example, for ternary AlCrN and TiAlN coatings the onset point of oxidation decreased to 600 °C with V incorporation [12, 24, 25]. In the case of the TiAlN/VN films, signals of lubricious $V_2O_5$ were detected as soon as the oxidation started (600 °C), while at high temperatures only AlVO$_4$ and TiO$_2$ were identified [12]. For AlCrVN coatings, AlVO$_4$, (Al, Cr, V)$_2$O$_3$ as well as $V_2O_5$ oxides were observed for an annealing temperature of 700 °C [25]. In these studies, the lower onset point of oxidation displayed by the V-containing coatings in relation to the host ones was explained by the reactions occurring between protective oxides and vanadium (such as formation of Al–V–O phases). Lower oxidation resistance of coatings due to V incorporation is not considered as a drawback from the tribological point of view, since the $V_2O_5$ oxide formed at the surface is known to reduce the friction and wear rate of coatings. Thus, as the oxidation behaviour strongly affects the performance of the coatings, some studies were conducted with the aim of understanding the diffusion processes occurring during coatings annealing. Zhou et al.
[24] and Franz et al. [25] studied TiAlN/VN and AlCrVN films, respectively. Zhou et al. [24] reported that a duplex oxide structure was formed during annealing of TiAlN/VN coatings for temperatures higher than 600 °C: an inner layer comprised a porous region of Ti rich and V rich nanocrystallites, while several phases were observed in the outer region, including V₂O₅, TiO₂ and AlVO₄. V₂O₅ phase was dominant in the outer surface at temperatures higher than 638°C. The outward diffusion of V depended on the species presented: in the inner layer, V was presented as V³⁺ and V⁴⁺, whilst V⁵⁺ was dominant in the outer layer. The porous inner layer was attributed to V ions diffusion to the surface to form V₂O₅. Franz et al. [25] also observed the formation of two different oxide layers during annealing of AlCrVN coatings. While vanadium diffusion led to a V-depleted inner oxide (mixed or nanocrystalline (Al,Cr,V)₂O₃), the outer oxide mainly contained V₂O₅ and small amounts of AlVO₄. Despite of these investigations, very little knowledge is still available for the static oxidation of V rich coatings.

Recently we have reported the effect of V incorporation on the structure, mechanical properties, oxidation resistance and tribological behaviour (at room temperature) of TiSiN films, deposited by DC reactive magnetron sputtering [26, 27]. TiSiN system exhibits similar level of oxidation resistance than AlCrN and TiAlN films [28, 29] (the only ternary films where the effect of V additions was studied); moreover, it can be deposited with much higher hardness depending on the structure and Si content. Lubricious vanadium oxides have been successfully detected on the oxidized surface and on the worn surface of these films, which decreased the wear rate and friction coefficient of coatings. However, as in the similar coating systems, a drop on the oxidation resistance of coatings was observed. In our specific case, the reaction of V with the protective oxide (Si-O) was not detected and therefore the decrease of the
oxidation resistance could not be attributed to such reactions. Present work provides a comprehensive understanding of the oxidation mechanism/diffusion processes occurring during TiSiVN films annealing. The effect of vanadium was studied in comparison to the diffusion processes occurring during annealing of a Ti$_{0.80}$Si$_{0.15}$N film, which were used as a reference. In addition, isothermal oxidation kinetics curves are included to provide a baseline.

2. Experimental procedure

TiSiN and TiSiVN coatings (labeled as Ti$_{0.80}$Si$_{0.15}$N and Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N, respectively), with approximately the same silicon content and about 2.5 µm of total thickness, were deposited on alumina and FeCrAl alloy substrates in a d.c. reactive magnetron sputtering machine equipped with two rectangular, Ti (99.9%) and TiSi$_2$ (99.9%), magnetron cathodes working in unbalanced mode. V incorporation was achieved by inserting 8 pellets of vanadium into the erosion zone of Ti target. In both cases Ti-V (0.24 µm) and Ti-VN (0.45 µm) adhesion layers were deposited as bonding layers improving coating to substrate adhesion. The depositions were performed with a negative substrate bias of 50 V. In both depositions, the total working gas pressure was kept constant at 0.3 Pa, using approximately 30 sccm of Ar and 17 sccm of N$_2$, and the deposition temperature was lower than 300 °C. These coatings were already characterized in our previous works [26, 27]. A summary of the deposition conditions and the main properties of the coatings are listed in Table 1. Temperature effect on the structure of the V rich coating was characterized in open air in-situ by hot-XRD device in the range of 500 °C to 750 °C, using a grazing incidence angle of 2° and Co Kα radiation (1.789010 Å). This range of temperature was selected based on the
thermogravimetric oxidation curves of films performed at a constant linear-temperature ramp (RT (room temperature) to 1200 °C at 20 °C/min) shown in Ref. [26]. Between each selected temperature a step of 10 min holding time was allowed for thermal stabilization and 30 min time acquisition was used. Oxidation of films was assessed by thermogravimetric analysis (TGA) using industrial air (99.99% purity). Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N and Ti$_{0.80}$Si$_{0.15}$N films were isothermally tested at 600 °C during 30 min and 900 °C during 1h, respectively. These temperatures represent main oxidation events observed in the previous thermal gravimetric oxidation curves performed at constant linear-temperature ramp [26]. After annealing, the cross section thin foils of oxidized films was prepared by focused ion beam (FIB) and analyzed by transmission electron microscope (TEM) equipped with an energy-dispersive x-ray (EDS) spectroscopy system. Bright field scan transmission electron microscopy STEM/EDX maps and elemental profiles along the cross section of the oxidized coatings were acquired to characterize the distribution of the main elements in the films (Ti$_{0.80}$Si$_{0.15}$N and Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N) and in the oxide scales.

3. Results and discussion

3.1 Characterization of the as-deposited and oxidized coatings

Firstly we will summarize the main characteristics and the oxidation resistance of Ti$_{0.80}$Si$_{0.15}$N and Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coatings. The investigated coatings with chemical composition of Ti$_{0.80}$Si$_{0.15}$N and Ti$_{0.65}$Si$_{0.11}$V$_{0.14}$N, showed a typical columnar morphology and fcc NaCl-type structure assigned to crystalline TiN with Si and V in solid solution [26]. V additions to the TiSiN coating significantly improved their
mechanical and tribological properties; however, their oxidation resistance was lowered. The improvement of the tribological properties was related to V-O formation in the sliding contact, which acted as a lubrrious tribo-film decreasing the friction and protecting the coating from wear [27]. Figure 1 shows the weight gain during isothermal oxidation at three selected temperatures. Note that Ti$_{0.80}$Si$_{0.15}$N film was tested at higher temperature than V rich coating since no signals of oxidation were detected at lower temperature. On the other hand, the oxidation resistance of the V rich coating could not be studied at 900 °C due to melting of V$_2$O$_5$ (~685 °C) [7, 13, 24] and consequent degradation of the film [26]. Ti$_{0.80}$Si$_{0.15}$N displayed a typical parabolic oxidation weight gain as a function of time, which indicates the presence of protective oxide scales. The isothermal curves of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N films tested at 550 °C and 600 °C showed two steps: they started with a linear increase in mass gain and then followed with a parabolic evolution. The surface morphologies of the oxidized coatings are shown in Fig. 1 b-c) for coatings Ti$_{0.80}$Si$_{0.15}$N tested at 900 °C and Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N oxidized at 600 °C, respectively. The detailed description of the surface oxide constitution, based on XRD diffraction, Raman spectroscopy and SEM-EDS analyses, can be found in our previous study [26]. Here we will briefly summarize these results to support the investigation aimed at diffusion process. Annealed Ti$_{0.80}$Si$_{0.15}$N film (see Fig. 1 b) exhibited two different surface features: white and dark gray islands evenly distributed on the surface. Raman analyses revealed that white phase was rutile (TiO$_2$), while dark gray phase was a mixture of rutile and anatase. However, only rutile peaks were detected by XRD diffraction suggesting very limited amount of anatase in the dark gray islands. Furthermore, strong signals of Si were detected on dark zone by EDS. However, the signals of silicon oxide were neither detected by XRD nor by Raman spectroscopy indicating amorphous character, which corroborates previous reports [30, 31]. Silicon
oxide was positioned below Ti-O rich layer. Different morphology and oxide phases were detected on the oxidized surface of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coating. At 600 °C, the film displayed a floret-like structure formed by light and dark gray phases. XRD diffraction showed the presence of α-V$_2$O$_5$ and Ti(V)O$_2$ oxides. Although EDS analysis revealed similar spectra for both phases, the much less intensity of the V peak on the light gray phase, and its conjugation with Raman analysis allowed identifying dark and light gray phases as α-V$_2$O$_5$ and Ti(V)O$_2$ oxides, respectively. Similarly to Ti$_{0.80}$Si$_{0.15}$N coating, signals from Si-O where neither detected by XRD nor by Raman spectroscopy. However, according to the EDS analyses this oxide should coexist with the Ti(V)O$_2$ phase as strong signals of Si coming from the sub-surface layer (light phase in Fig. 1c)). Similar phases were detected at 550 °C by XRD; however, only small dark gray areas were observed at the surface.

3.2 Phase evolution during annealing of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N (in situ) and growing mechanism of the V$_2$O$_5$ phase

Fig. 2 plots the high temperature in-situ XRD spectra evolution for Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coating together with as deposited and cooled state. The first signs of oxides were detected at 500 °C and identified as rutile type phase with V in solid solution, the Ti(V)O$_2$ (ICDD card 77-0332). Further increase in temperature to 550 °C led to an increase of the Ti(V)O$_2$ peaks intensity and the appearance of a new phase: the α-V$_2$O$_5$ (ICDD card 41-1426) oxide with orthorhombic symmetry (peak at 23.6°). At 600 °C a strong increase in intensity of the α-V$_2$O$_5$ oxide peaks with a strong preferred orientation following the (001) plane was observed. Moreover, a metastable phase was formed, β-V$_2$O$_5$, as a result of oxygen loss from α-V$_2$O$_5$ due to a reduction process [32].
It should also be pointed out that the higher intensity of $V_2O_5$ peaks in relation to other peaks suggests higher quantity on the oxidized volume. The temperature increase to 650 °C led to suppression of TiN peaks suggesting the formation of a thick oxide scale. At 675 °C, the peaks associated with the $V_2O_3$ phases disappeared, which was in a good agreement with the melting point of $V_2O_5$ oxide [7, 13, 24]. On the other hand, peaks related to a $V_3O_5$ phase, which resulted from the $\alpha$-$V_2O_5$ reduction, were found. In fact, in case of oxygen deficiency, a shift to lower valence state leads to the formation of reduced oxides, such as $V_3O_5$ identified in the current XRD pattern. Further increase in temperature resulted mostly in the increase of $V_3O_5$ peaks intensities due to continuous reduction of liquid $V_2O_5$ phase. Ti(V)O$_2$, $V_2O_5$, $V_2O_3$ and VO reduced phases were found after annealing, as well as a new polymorph $V_2O_3$ oxide: $\gamma'$- $V_2O_5$ (ICDD card 85-2422). This oxide has an orthorhombic structure as $\alpha$-$V_2O_5$ phase, but with different diffraction planes. These changes could be attributed to distortions on the structure motivated by the cooling of liquid-phase. Double chains exist in both phases, but VO$_5$ pyramids alternate up and down individually for $\gamma'$- $V_2O_5$, whereas they alternate by pairs for normal $\alpha$-$V_2O_5$ phase [33]. These results are in a good agreement with the oxide phases previously identified on the oxidized surface of the film.

The growth mechanism of the $V_2O_5$ phase over the Ti(V)O$_2$ oxide on the oxidized surface of the V rich film is shown in Fig. 3. SEM/EDS analyses revealed that nucleation points of $V_2O_5$ started being formed over the oxidized surface (see peak ID 2), growing up by vanadium lateral diffusion as suggested by the EDS spectra obtained from the V depleted white and V rich black regions marked in the SEM micrograph (zones 3 and 4, respectively). In order to investigate the oxide scale growth, TEM cross-sections were prepared by FIB from Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N and Ti$_{0.80}$Si$_{0.15}$N films annealed at 600 and 900 °C, respectively. It should be emphasized here that the different oxidation
isothermal temperatures were used due to dissimilarities in the oxidation resistance of coatings as referred to above.

3.3 Cross section of oxidized surfaces by TEM and oxidation kinetics

Fig. 4 and 5 displays the bright-field STEM images, associated elemental maps and scanning elemental profiles from cross section of oxidized Ti$_{0.80}$Si$_{0.15}$N and Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coatings. In the case of Ti$_{0.80}$Si$_{0.15}$N film a multilayer of oxides can be identified, being more complex close to the film defect (white zones) shown in Fig. 4a): (i) an outer Ti-rich layer comprised by shaped crystals with bigger size in the top of the film defect, zone corresponding to the white phase and, (ii) a Si-rich layer, which is itself divided in 3 layers on the zone around the defect, an intermediate layer containing Ti, sandwiched between two Ti-free layers, being the external porous and the internal one very compact. Far from the film defect (left zone of the micrograph), below to the TiO$_2$ crystals only a homogeneous Si-rich layer was observed. The measured elemental cross-section depth profiles for two lines were plotted in Fig. 4b) and 4c), respectively. The profiles corroborated STEM/EDX elemental mapping showing in detail the composition of surface oxides. The surface layer formed exclusively of Ti-O was followed by a Si-rich layer with scattering in the signals intensity, in agreement with brightness intensity in figures 4 a). It is clear in Ti-signal a small increase in intensity in the zone of high-Si content. This variation is more intense in line 2 than in line 1, suggesting an influence of the film defect, which is closer to line 2. Continuous and compact Si-O layer at the oxide/coating interface acts as an efficient barrier against oxygen and metal ions diffusion and thus protecting the coating from further oxidation [30, 31].
It is evident that Ti oxide forms first on the surface of the film due to the higher affinity of Ti for O than Si [30, 31] and then, with further increase in temperature, silicon oxide is formed due to the progressive segregation of Si. The oxidation process will then occur through the inwards diffusion of O\(^2\^-\) through the TiO\(_2\) layer and the outwards diffusion of Ti\(^{4+}\) through the Si-O layer [34]. Nevertheless, due to the presence of film defects, in the first stage of the oxidation process, a high amount of Ti ions will be supplied in that zone corresponding to the oxidation occurring in the defect walls. This process will promote the formation of a porous Si-O layer, with low diffusion barrier performance to the out diffusion of Ti\(^{4+}\) ions, leading to large TiO\(_2\) crystals on the oxide scale surface. From the moment that a Si-O barrier layer is formed in the defect walls (see Si signal in figure 4 a)) the oxidation process will be controlled by the O\(^2\^-\) inward and Ti\(^{4+}\) outward ions diffusion through the Si-O layer [34]. It should be remarked that this phenomenon should not influence significantly the global oxidation behaviour of the Ti-Si-N coating (which shows the parabolic behavior presented in Fig. 1 a), in agreement with literature [30, 31, 34]) since, on the one hand, it only occurs in a few defects in the films surface (see Fig. 1 b)) and, on the other, it should be more intense in the first stage of the oxidation, during heating up to the 900 °C isothermal oxidation temperature.

Ti\(_{0.65}\)Si\(_{0.11}\)V\(_{0.15}\)N coating exhibited, after annealing, two-layers oxide structure with a thick porous inner layer and an outer discontinuous layer of well-defined crystals. The elemental maps shown in Fig. 5a) suggested that the majority of vanadium was located in the outer crystal layer, whereas inner layer was Ti and Si rich. These results corroborates the detection of the rutile type compound Ti(V)O\(_2\) and V\(_2\)O\(_5\) indexed by XRD and Raman spectroscopy in the light and dark phases in Fig. 1 c) [26], for the sub-surface and top oxide layer respectively. Further, the presence of Si-O at the
sub-surface is in agreement with the EDS results shown in our previous work [26]. Elemental lines shown in Fig. 5b) and 5c) showed that diffusion of V occurred exclusively within the oxidized volume, since V is almost completely depleted in the inner oxide layer whereas no V gradient is detected in the non oxidized coating, as shown by the constant V signal across this zone. In general, we observed a thicker non oxidized layer in the regions covered by V-O crystal phase. Furthermore, comparing either the V content integrated intensities of Fig. 5a) and b) or the brightness of V signal between the right and left part of Fig. 5 a), it can be concluded that V has to be diffused from the left to the right zone of this figure. Finally, it should be remarked that there is no indication of formation of any Si-rich layer, being Si signal uniformly distributed in both oxide scale and non-oxidized coating. Therefore, a dense compact protective silicon oxide layer localized in subsurface was not formed being Si-O randomly distributed in the Ti(V)O_2 porous scale.

Isothermal curve of Ti_{0.65}Si_{0.11}V_{0.15}N coating oxidized at temperatures below the melting point of V_2O_5 started with a linear increase in mass gain obeying after that to a parabolic law. A strong correlation can be found between the microstructure of the oxide scale and the isothermal oxidation curve of Ti_{0.65}Si_{0.11}V_{0.15}N coating. High temperature XRD patterns shown in Figure 2), revealed that the first oxide being formed is Ti(V)O_2. At the very beginning of the oxidation process, due to the high Ti content, a TiO_2 layer starts growing. The presence of V ions and its high solubility with Ti promote the formation of Ti(V)O_2 solid solution, which comprises vanadium cations with lower oxidation states as V^{3+} ions [15, 35]. The substitution of Ti^{4+} by V^{3+} ions in the TiO_2 lattice would increase the concentration of interstitial metallic Ti^{4+} ions and decrease the number of excess electrons and consequently increasing the oxidation rate. This justifies the initial rapid oxidation observed in the isothermal curve, in good
agreement to the work of Thongtem et al. [35] who studied the effect of V doping to Ti-based alloys. At the same time that Ti(V)O$_2$ oxide is being formed, Si ions are being supplied at the interface to form Si-O. However, due to V ions diffusion through the oxide scale to the surface, the formation of a protective and compact Si-O layer is inhibited, degrading the oxidation resistance of the coatings when compared to Ti$_{0.80}$Si$_{0.15}$N film. This agrees well with the elemental maps shown in Figure 5 a), where Si-O and Ti(V)O$_2$ coexist in the inner porous layer, never showing a continuous agglomeration of Si-O necessary to protect the material from oxidation. Such observations are in accordance to literature works on diffusion processes of V rich coatings, where an inner porous layer was always formed due to V ions migration to the surface (Refs. [24, 25]). From the moment that vanadium cations, with lower oxidation states, (V$^{3+}$ or V$^{4+}$) arrive to the surface, they are further oxidized to V$^{5+}$ combining with O ions and creating nucleation points for the V$_2$O$_5$ growth, which will expand and grow up by vanadium lateral diffusion, as evidenced in Fig. 3. With the ongoing oxidation, the oxide scale became thicker and the isothermal curve started to obey to a parabolic law due to a reduction of ions mobility through the oxide scale. The process develops leading to the formation of a porous rich inner Ti(V)O$_2$ and Si-O layer and an outer most dispersed V$_2$O$_5$ one, that can comprise both α-V$_2$O$_5$ and β-V$_2$O$_5$ phases as evidenced in the XRD patterns at high temperature.

4. Conclusion

In this investigation, the effect of V additions on the oxidation and diffusion processes occurring during Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N film annealing is studied and related to the behaviour of ternary Ti$_{0.80}$Si$_{0.15}$N system. In summary, we demonstrated that oxidation of
Ti$_{0.80}$Si$_{0.15}$N is controlled by the formation of a dense and compact silicon oxide acting as a diffusion barrier, which can be affected by defects in the as-deposited film. The presence of V cations with lower oxidation states in the TiO$_2$ scale, during the oxidation of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N film, was responsible for a significant increase of the oxidation rate and the inability of formation of a Si-O protective oxide.

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References


Figure Captions

Figure 1 – a) Isothermal oxidation curves of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coating tested at 600 ºC during 30 min and 550 ºC during 1h and Ti$_{0.80}$Si$_{0.15}$N coating tested at 900 ºC during 1h, b-c) typical surface morphologies of Ti$_{0.80}$Si$_{0.15}$N and Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coatings annealed at 900 ºC during 1h and 600 ºC during 30 min, respectively.

Figure 2 – XRD spectra of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N film at different temperatures (upper) and position of main peaks of corresponding phases (lower).

Figure 3 – a) Oxidized surface of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coating isothermal tested at 550 ºC during 30 min, showing the growing mechanism of V$_2$O$_5$ phase. SEM/EDS spectra of: b) point 1, c) point 2, d zone 3, e) zone 4.

Figure 4 – a) bright field STEM cross section and correspondent elemental maps of Ti$_{0.80}$Si$_{0.15}$N coating oxidized at 900 ºC during 1h. Elemental line scans along the cross section of the oxidized coating obtained from two places: b) line 1, c) line 2.

Figure 5 – a) bright field STEM cross section and correspondent elemental maps of Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coating oxidized at 600 ºC during 30 min. Elemental line scans along the cross section of the oxidized coating obtained from two places: b) line 1, c) line 2.
Figure 1a
Figure 1b
Figure 1c
Figure 2
Figure 3a

Floret-like $\text{V}_2\text{O}_5$ phase
Figure 3b
Figure 3c
Figure 3d
Figure 3e
Figure 4a
Figure 4b
Figure 4c
Figure 5a
Figure 5b
Figure 5c
Table 1 - Designation, deposition conditions and main properties of the Ti$_{0.80}$Si$_{0.15}$N and Ti$_{0.65}$Si$_{0.11}$V$_{0.15}$N coatings.

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<th>TiSiVN</th>
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<td>6 1.5</td>
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</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>307 ± 10</td>
<td>328 ± 7</td>
</tr>
<tr>
<td>Residual stresses (GPa)</td>
<td>3.4</td>
<td>4.1</td>
</tr>
<tr>
<td>Onset point of oxidation</td>
<td>900 °C</td>
<td>500 °C</td>
</tr>
<tr>
<td>Friction coefficient (room temperature) against Al2O3</td>
<td>1.07</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Research highlights

- V additions increased the oxidation rate of TiSiN films.
- Oxidation of TiSiN films is controlled by ions diffusion though a Si-O layer.
- In TiSiVN case, the Si-O layer growth is inhibited by V outward ions diffusion.
- V$_2$O$_5$ phase formed over the oxidized surface grows by lateral V ions diffusion.