Towards hard yet self-lubricious CrAlSiN coatings

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A B S T R A C T

CrAlSiN coatings are of high hardness, excellent wear and oxidation resistance but lack of lubriciousness. Vanadium nitride (VN) is easily oxidized to form vanadium oxides and becomes lubricious under stress. Incorporating VN into CrAlSiN to form CrAlSiVN coating renders both hardness and self-lubrication in dry machining. This study investigates the effect of vanadium content on hard yet self-lubricious coating's mechanical and tribological properties. The coatings are deposited on cemented tungsten carbide and Si wafer (100) substrates in an in-line magnetron sputtering system. Grazing incidence X-ray diffractometer, scanning electron microscopy, transmission electron microscopy, electron probe micro-analyzer, X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy are employed to characterize the microstructures and chemistry. Nanoindentation and ball-on-disc tribo-tester are used in characterization of the mechanical and tribological properties. The coatings demonstrate lubriciousness of coefficient of friction with tungsten carbide and Si wafer (100) substrates in an in-line magnetron sputtering system. Grazing incidence X-ray diffractometer, scanning electron microscopy, transmission electron microscopy, electron probe micro-analyzer, X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy are employed to characterize the microstructures and chemistry. Nanoindentation and ball-on-disc tribo-tester are used in characterization of the mechanical and tribological properties. The coatings demonstrate lubriciousness of coefficient of friction with tungsten carbide and Si wafer (100) substrates in an in-line magnetron sputtering system. Grazing incidence X-ray diffractometer, scanning electron microscopy, transmission electron microscopy, electron probe micro-analyzer, X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy are employed to characterize the microstructures and chemistry. Nanoindentation and ball-on-disc tribo-tester are used in characterization of the mechanical and tribological properties. The coatings demonstrate lubriciousness of coefficient of friction with tungsten carbide and Si wafer (100) substrates in an in-line magnetron sputtering system.

1. Introduction

Traditional cutting using lubricant cooling not only washes away dollars thus jags up the cost of the work piece but also causes damage to the environment thus dry or semi-dry cutting are proposed and subsequently applied to cutting processes in the last decade [1]. However, dry machining also poses great challenges to cutting tools [2]; during machining the metals, especially soft metals, exhibit high friction and strong adhesive interaction with tool materials therefore a strong tendency of generating built-up edges (BUE). BUE is the main reason for high cutting force and temperature, low machining accuracy and short tool life [3]. To overcome BUE, the machine tools should be lubricious as well as hard and strong. Coating is an efficient way out. The interest in hard coatings for high speed and dry cutting applications has grown rapidly, among which CrAlSiN coatings have attracted much attentions. Silicon introduced into the CrAlN coatings can form a strongly immiscible system, where Si segregates as amorphous SiN\textsubscript{x}, along the grain boundaries and form sharp and strong interfaces which can significantly affect the grain size [4,5]. The absence of dislocation activity in the small nanocrystals and blocking the grain boundary sliding by the formation of a strong interface between the two phases provide the nanocomposite materials with superior properties such as high hardness, good wear and excellent oxidation resistance [6,7]. However, their friction coefficients are fairly high [8,9] thus hinders its application in dry machining. Doping lubricant into the CrAlSiN system is an effective way out. Conventional solid lubricant like diamond like carbon, MoS\textsubscript{2}, and h-BN fail due to oxidation under extreme conditions like ambient moisture and elevated temperatures [10], therefore are not suitable for dry machining.

Vanadium oxides melt at approximately 685 °C [11] thus becomes ‘lubricious’ under stress and temperature. Series of V-based hard coatings have been developed, such as (V, Ti) N [12,13], CrVN [14], CrAlVN [15,16] composite coatings, AlN/VN [17,18], CrAlIN/VN [19] and TiAlN/VN [3,20,21] multilayer coatings with good mechanical and tribological properties. In TiAlN/VN multilayer coatings, melting of VO\textsubscript{x} at 700 °C gives rise to low friction coefficient of 0.18 [20]. In our previous study, CrN/VN multilayer coatings demonstrated low coefficient of friction (COF) of 0.21 due to formation of VO\textsubscript{x} during tribo-test at room temperature [22]. Logically, the combination of CrAlSiN and VN should provide an alternative for a hard and lubricious coating for dry machining.

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The aim of this work is to explore the effectiveness of the incorporation of V into the CrAlSiN matrix to prepare CrAlSiVN coatings. Main emphasis is laid on the determination of the microstructure and mechanical properties of the coatings and the evidence of low-friction effect. With proper vanadium content, the coatings are hard yet self-lubricious.

2. Experimental

2.1. Deposition of the coatings

Four CrAlSiVN coatings (labeled as V0 to V3) with constant Si content were co-deposited on polished VT15 cemented tungsten carbide (WC + 15 wt.% TiC + 6 wt.% Co) and silicon wafer (100) substrates in an in-line reactive magnetron sputtering system (PSUVHL-200C, HOPE Vacuum Technology Co., Ltd., Taiwan). The sputtering targets are CrAl alloy (Cr: 70 at.%, Al: 30 at.%), pure Si (99.99 wt.% purity) and pure V (99.99 wt.% purity) of 152.4 mm in diameter. Prior to deposition, the sputtering targets are CrAl alloy target power density of 2.48 W/cm², and the silicon target power density was set as 3.58 W/cm². Before deposition took place, a 15 min plasma etching was conducted at a bias voltage of −0.4 Pa under substrate bias of −180 V. The total gas flow was kept at 40 sccm. The radio frequency (RF, 13.56 MHz) induced negative bias voltage was set at 180 V. The total processing pressure was maintained at 0.4 Pa with Ar flow rate of 20 sccm and N₂ flow rate of 0.5 Pa and the processing pressure was maintained at 0.4 Pa with Ar flow rate of 20 sccm and N₂ of 20 sccm. To assess the influence of vanadium alone, Si content is kept constant, and the silicon target power density was set as 3.58 W/cm²; the vanadium target power density was enhanced from 0 to 2.48 W/cm², and the CrAl alloy target power density was reduced from 1.65 W/cm² to 0.83 W/cm² simultaneously, to control the element contents in the composite coatings. During deposition, the substrate temperature was kept at 400 °C. The substrate holder was allowed to rotate steadily in order to guarantee the homogeneous feature along the surface plane. The radio frequency (RF, 13.56 MHz) induced negative bias voltage was set at −180 V. The total thicknesses of coatings were controlled at around 1 μm. Before deposition took place, a 15 min plasma etching was conducted at a bias voltage of −300 V to remove oxides and contaminants on the surface. The designation and typical deposition conditions were listed in Table 1. VN monolayer coatings were also prepared with target power density of 2.48 W/cm² and tested as reference.

2.2. Coating characterization

The composition of coatings was evaluated using Field Emission Electron Probe Micro-Analyzer (FE-EPMA, JEOL JXA-8500F) with the aid of the ZAF-corrected pro-

Table 1
Deposition parameters and thickness of the coatings.

<table>
<thead>
<tr>
<th></th>
<th>V0</th>
<th>V1</th>
<th>V2</th>
<th>V3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target power density (W/cm²)</td>
<td>CrAl</td>
<td>V</td>
<td>Si</td>
<td>V</td>
</tr>
<tr>
<td>CrAl</td>
<td>1.65</td>
<td>1.38</td>
<td>1.10</td>
<td>0.83</td>
</tr>
<tr>
<td>V</td>
<td>–</td>
<td>1.10</td>
<td>1.93</td>
<td>2.48</td>
</tr>
<tr>
<td>Si</td>
<td>3.58</td>
<td>3.58</td>
<td>3.58</td>
<td>3.58</td>
</tr>
<tr>
<td>Base pressure (Pa)</td>
<td>&lt;4 x 10⁻⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasma etching</td>
<td>Ar plasma for 15 min at 0.4 Pa under substrate bias of −300 V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interlayer</td>
<td>40 nm thick CrAl interlayer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working pressure (Pa)</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar: N₂ gas ratio</td>
<td>1: 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total gas flow (sccm)</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RF substrate bias (V)</td>
<td>−180 (13.56 MHz)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coatings thickness (nm)</td>
<td>955</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice constant (nm)</td>
<td>0.4223</td>
<td>0.4143</td>
<td>0.4143</td>
<td>0.4131</td>
</tr>
</tbody>
</table>

Table 2
Chemical concentration of the coatings.

<table>
<thead>
<tr>
<th>Coatings</th>
<th>Cr</th>
<th>Al</th>
<th>N</th>
<th>Si</th>
<th>V</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>V0</td>
<td>31.9</td>
<td>17.3</td>
<td>42.5</td>
<td>7.8</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>V1</td>
<td>25.2</td>
<td>13.6</td>
<td>43.5</td>
<td>7.4</td>
<td>9.2</td>
<td>1.4</td>
</tr>
<tr>
<td>V2</td>
<td>19.6</td>
<td>10.5</td>
<td>42.1</td>
<td>6.9</td>
<td>19.5</td>
<td>1.4</td>
</tr>
<tr>
<td>V3</td>
<td>15</td>
<td>8.2</td>
<td>41.1</td>
<td>8.0</td>
<td>25.8</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Fig. 2. Grain size of the coatings as determined by GIXRD through Williamson–Hall equation.

\[
\beta_{\text{hl}} \cos \theta_{\text{hl}} = \frac{K \lambda}{D} + 4\varepsilon \sin \theta_{\text{hl}}
\]
Nanoindentation tests were carried out at a maximum load of 5 mN with a nanoindenter (TI-900, Tribo-Indenter, Hysitron, USA) equipped with a Berkovich diamond tip angled at 142.3°. Eight indentations were made for each coating. The maximum indentation depth was limited to around 50 nm, which was less than the one-tenth of the coating thickness. Ball-on-disc wear test was carried out through a tribo-tester (Tribo-meter, J&L Tech Co., Ltd., Korea) to characterize the tribological performances. A tungsten carbide (WC) ball (hardness of 89.5–91.0 HRA, surface roughness of 0.063–0.080 μm, and 6 mm in diameter) was adopted as the stationary ball. The normal load and sliding distance were 5 N and 1000 m, respectively, which were enough to create wear scars. The sliding linear speed was 84 mm/s at radius of 4 mm. The test temperature was 24°C, and the relative humidity was about 65%. The friction coefficient was determined from friction-wear distance curves after 50 m running-in period to minimize the influence from surface topology [24]. The wear scars were characterized by scanning electron microscopy (SEM, HITACHI S3400 N, Japan) at 15 kV. The wear debris was also examined with X-ray Photoelectron Spectroscopy (XPS, Kratos, Britain) for chemical bonding using Al Kα (1486.71 eV) radiation (10 mA and 15 kV). The wear rate of the coating was determined based on the following equation [25]:

\[
W_R = \frac{t(3r^2 + 4b^2)2\pi}{6b^3}
\]

where \( t \) is the depth of the wear track determined by a surface profilometer (Kosaka Surfcorder ET3000, Japan), \( b \) is the width of the wear track determined by SEM, \( r \) is the radius of the wear track, \( F_n \) is the normal load and \( S \) is the sliding distance. The wear volume of the coupled ball was evaluated with an optical microscope, measuring the diameter of the wear scar formed on the coupled ball and assuming that the wear scar is perfectly circular and flat in order to simplify the calculations. The wear volume of the coupled ball divided by sliding distance and load can get the wear rate. High-temperature wear test against Al₂O₃ ball (3 mm in diameter, Moh’s hardness of 9, surface roughness of around 0.2 μm) was performed in air at 700°C on
a ball-on-disc high-temperature tribometer (CSM Instruments SA, Switzerland). The test conditions were: a normal load of 2 N, wear track of 2.5 mm diameter, rotation speed of 84 mm/s and sliding distance of 200 m. The friction coefficient and wear rate of coatings were estimated as mentioned above. The coatings and wear scars after 700°C tribo-test were examined by energy dispersive X-ray spectroscopy (EDX, JEOL, JSM-6380LV, Japan) chemical analysis at 20 kV.

3. Results and discussion

3.1. Chemical composition and microstructure

The chemical compositions of the coatings determined by EPMA analysis are listed in Table 2. It is confirmed that silicon, nitrogen have approximate constant content of (7.5 ± 0.4) and (42.3 ± 0.9) at.%, respectively. With vanadium target power density enhancing, the contents of vanadium in coatings increase from 0 to 9.2, 19.5 and 25.8 at.%, that of chromium and aluminum decreases simultaneously which agree well with the design.

Fig. 1 presents the GIXRD patterns of the coatings. Face-centered-cubic (FCC) structure is confirmed from the diffraction peaks of (200), (220), (311) and (222). CrAlSiN coating presents weak (311) and (222) peaks. The VN coating has a strong (200) peak and weak (220), (311) peaks. After vanadium doped into coatings, strong (200) and weak (220), (311), (222) peaks are observed in CrAlSiVN coatings. As vanadium content increasing, understandably, VN influences the growth direction of the composite coatings, giving rise to (200) texture. And no peaks corresponding to crystalline silicon nitride or silicon can be identified.

![Fig. 5. TEM images and the inserted SAED pattern: (a) V0 and (b) V3.](image)

![Fig. 4. Cross-sectional morphologies of the coatings.](image)

![Fig. 6. Nanoindentation hardness of as-deposited coatings.](image)
The grain sizes of the coatings as determined from GIXRD through Williamson–Hall equation [23] are plotted in Fig. 2. After vanadium is introduced into the coatings, the grain sizes decreases from 10.3 nm to 6.0 nm. Similar phenomenon can be found in Baran’s work [26] which named “micro-alloying” effect. Since the Gibbs free energy of VN is –191.1 kJ/mol, and that of CrN is –93.0 kJ/mol [27], when vanadium is doped into the coatings, comparing with chromium, vanadium bonds with nitrogen more easily, and the nuclear rate is accelerated, thus the grain sizes are refined.

From the Bragg equation [28],
\[
2d_{\text{hkl}} \sin \theta = n \lambda
\]
where \( \lambda \) is wavelength of X-rays, \( \theta \) is diffraction angle, \( h \), \( k \), and \( l \) are the Miller indices; the inter-planar spacing (\( d_{\text{hkl}} \)) for the plane \((hkl)\) in CrAlSiN and CrAlSiVN coatings could be obtained.

The cubic lattice parameter \( a \) for the cubic phase structure is determined by the Eq. (4) [28]:
\[
a = d_{\text{hkl}}(h^2 + k^2 + l^2)^{1/2}
\]
The corrected values of lattice parameter (lattice constant: \( a_0 \)) could be estimated from the Nelson–Riley function [28]:
\[
a = a_0 + K \frac{\cos^2 \theta}{\sin \theta}
\]
Eq. (5) represents a straight line between \( \frac{\sin \gamma}{\cos^2 \gamma} \) (X-axis) and \( a \) (Y-axis). The slope of the line gives the \( K \). The intercept of this line on Y-axis gives the \( a_0 \) and tabulated in Table 1, and that of VN is 0.4134. The lattice constant of CrAlSiN coating is 0.4223 which is larger than that of CrN (PDF card #65-2899, \( a_{\text{CrN}} = 0.4149 \)) signifying part of the doped Al or Si acting as interstitial atom in CrN lattice structure. After vanadium is introduced into the composite coatings, with vanadium content increasing, the lattice constant \((0.4143, 0.4143, 0.4131 \, \text{nm}, \text{respectively for V1 through V3})\) is approaching to that of VN. As the lattice constant of the composite coating is nothing but a weighted average of the constituents of the coating, dominating VN understandably results the composite coating’s lattice aligning towards that of the VN.

Fig. 3 shows the elemental bonding states of the V3 coating (with vanadium content of 25.8 at.%). Cr bonds with N seen as from the peaks centered at 575.7 eV [29] (Fig. 3(a)). N bonding with Cr and Al is observed from N 1s narrow scan, in which N is also partially bonded with Si and V [29] (Fig. 3(b)). Si–N bonding is confirmed from the Si 2p\(_{3/2}\) peak (Fig. 3(c)) centered at 101.6 eV [29]. No pure Si (99.0 eV) or Si–O (103.9 eV) [29] bonds can be observed, indicating Si entirely bond with N. Nevertheless, no diffraction peaks of SiN\(_x\) are observed in XRD patterns, implying that the SiN\(_x\) phase may form amorphous features in CrAlSiVN coatings. In V 2P\(_{3/2}\) peak (Fig. 3(d)), binding energy of 514.1 eV, 515.6 eV and 517.0 eV are assigned to VN, V\(_2\)O\(_3\) and V\(_2\)O\(_5\) respectively [29,30]. At room temperature, VN is typically oxidized several atomic layers following the so-called “low-temperature oxidation” mechanism [31]. Since XPS technique is only sensitive to a depth of about 10 nm [32], the V\(_2\)O\(_3\) percentage result thus only reflects the ratio within the XPS detectable depth, not the V\(_2\)O\(_3\) bulk content of the coating. Al 2p (Fig. 3(e)) centered at 74.2 eV [29] indicates Al is bonded with N.

Fig. 4 shows the cross-sectional morphologies of the composite coatings. All the coatings reveal fine compact structure without obvious columnar. The thicknesses of the coatings are about 930 nm to 958 nm obtained from the FE-SEM images and listed in Table 1. The thickness of CrAl interlayer is about 40 nm.

The TEM images and selected-area electron diffraction (SAED) patterns of V0 and V3 coatings are presented in Fig. 5(a) and (b). Columnar grain about 20 nm in width is found from V0 coating (Fig. 5(a)). In V3 (Fig. 5(b)), nano-grains (grain size less than 10 nm) replace the columnar structure which also proves the results from XRD. The “micro-alloying” effect from vanadium leads to a repeated nucleation and resulting in smaller globular grains. In

![Fig. 7. Coefficient of friction and wear scar of the coatings after ball-on-disc tribo-test.](image-url)

![Fig. 8. XPS spectra of V 2p\(_{3/2}\) of the wear debris of V3 coating.](image-url)
with vanadium content of 19.5 at.%; when it further increases to 25.8 at.%, the COF declines to 0.39. Wider wear scar can be found from V1 and V2 (with vanadium content of 9.2 at.% and 19.5 at.%), and then becomes narrow in V3. More wear debris can be found from the wear track of V1 and V2. Those coatings possess higher COF corresponding to lower hardness and low vanadium content. During tribo-test, the coatings with poor hardness will be easily scuffed, inducing rougher surface; additionally, lower vanadium content corresponds to less tribo-lubricant in wear debris, thus results high COF. Fig. 8 illustrates the XPS V2p 3/2 spectra of the wear debris of V3 coating after tribo-test. VN, V2O3, and V2O5 also can be detected in wear debris. VOx has easy slipping shear planes \([10,34,35]\) which acts as lubricant during tribo-process and results in lower COF, especially in V3 coating (with 25.8 at.% vanadium). Fig. 9 shows the wear rate of coatings and coupled WC balls after tribo-test. The wear rate of CrAlSiN coating is \(3.08 \times 10^{-7}\) mm\(^3\)/Nm. After vanadium doped into the coatings, the wear rate increases to \(4.41 \times 10^{-7}\) and \(6.50 \times 10^{-7}\) mm\(^3\)/Nm (V1 and V2, separately). But, when vanadium content is 25.8 at.% (V3), the wear rate descends to \(5.16 \times 10^{-7}\) mm\(^3\)/Nm. The tendency between wear rate and vanadium content is similar with the COF. Coating with lower hardness is easier to be worn. For V3, high content vanadium brings a self-lubricious effect, and thus, descends the wear rate. After vanadium is introduced into CrAlSiN coating, the wear rates of WC ball decreases from \(1.08 \times 10^{-7}\) mm\(^3\)/Nm to \(8.60 \times 10^{-7}\) mm\(^3\)/Nm (V0 to V3). According to the hardness of the nitrides, harder the coating is, more of the ball is worn.

The COF and wear rate of the coatings with alumina at 700 °C are shown in Fig. 10(a) and (b). The COF of CrAlSiN coating is 0.66. Similar with the tendency of COF at room temperature, the COF of the nitrides peaks at 0.71 with vanadium content of 19.5 at.%, and then, descends to 0.67 with vanadium content of 25.8 at.%. With vanadium content increasing, the wear rate of the coatings increases from \(2.67 \times 10^{-6}\) mm\(^3\)/Nm (V0) to \(14.67 \times 10^{-6}\) mm\(^3\)/Nm (V2); but for V3, the wear rate declines to \(8.60 \times 10^{-6}\) mm\(^3\)/Nm. The tungsten and oxygen contents from coating and wear scar after 700 °C tribo-test are tabulated in Table 3. All of the coatings are partially worn out with tungsten content increases from around 2 at.% (in coatings) to around 30 at.% (in wear scars). With vanadium content increasing, oxygen content in coatings rises from 5.31 at.% (V0) to 29.32 at.% (V3), means doping vanadium aggravates coating’s oxidization, which may impact coating’s high—temperature hardness and cutting ability. Nevertheless, high content of vanadium supplies enough VOx lubricant and induces lower COF and wear rate at 700 °C for V3 comparing with V2.
4. Conclusions

Incorporating vanadium into CrAlSiN structure refines its grains and brings a slight drop of hardness: from about 35 GPa down to 30 GPa when V content increases from 0 to 25.8 at.%. Meanwhile, however, coefficient of friction (COF) against tungsten carbide drops from 0.55 down to 0.39 at room temperature; and the COF against alumina drops from 0.71 down to 0.67 at 700°C.

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