Self-lubricating CrAlN/VN multilayer coatings at room temperature

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ABSTRACT

Vanadium nitride (VN) is easily oxidized to form vanadium oxides and becomes lubricious under stress. CrAlN is hard thus CrAlN/VN multilayer coatings render both hardness and lubricious properties attractive in dry machining of soft metals. This study investigates the effect of multi-layering on the coating's mechanical and tribological properties at room temperature. The CrAlN/VN multilayer coatings are deposited on cemented tungsten carbide and Si wafer (1 0 0) substrates in an in-line magnetron sputtering system. A period contains one layer of CrAlN plus one adjacent layer of VN. The period thickness varies roughly from 3 nm to 30 nm; the total number of the periods varies from 30 to 300. X-ray diffractometry, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and electron probe micro-analyzer are employed to characterize the microstructures and chemistry. Nanoindentation and ball-on-disk wear test are used in mechanical and tribological studies. The CrAlN/VN multilayer coatings have good lubricant property with lowest coefficient of friction of 0.26. At the period thickness of 20 nm, the multilayer coatings obtained the best mechanical properties (hardness of 32.4 GPa, elastic modulus of 375 GPa, minimum wear rate of 1.1 × 10^{-7} mm\textsuperscript{3}/Nm).

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1. Introduction

Dry machining is environmentally friendly and cost effective which becomes more and more popular. However, dry machining also poses great challenges to cutting tools [1] on soft metals such as aluminum alloys. During machining, the 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, poor surface finish and short tool life [2]. To overcome BUE, the machine tools should be lubricious as well as hard and strong. Coating is an efficient way out. However, transition metal nitride coatings like TiN, TiAlN and CrN perform poorly due to high coefficient of friction [2–4]; conventional solid lubricating coatings like diamond like carbon, MoS\textsubscript{2}, and h-BN fail due to oxidation under extreme conditions like ambient moisture and elevated temperatures [5]; thus they are not suitable for dry machining.

Recently, vanadium nitride (VN) has attracted increasing interests as VN is easily oxidized to form Magnéli-phase vanadium oxides have easy slipping shear planes [5–7] and melt at approximately 685 °C [8] thus becomes 'lubricious' under stress and temperature. Series of V-based hard coatings have been developed, such as (V, Ti) N [9,10], CrVN [11], CrAlVN [12,13] composite coatings, AlN/VN [14,15] and TiAlN/VN [2,16,17] multilayer coatings with good mechanical and tribological properties. In TiAlN/VN multilayer coatings, melting of VO\textsubscript{2} at 700 °C gives rise to low friction coefficient of 0.18 [16]. In our previous research, CrN/VN multilayer coatings demonstrated low coefficient of friction (COF) of 0.21 due to formation of VO\textsubscript{2} during tribo-test at room temperature [18]. CrAlN coatings have good oxidation resistance, anticorrosive and anti-adhesive properties [19–21], but inadequate tribological resistance hinders their applications in dry machining. Logically, the combination of CrAlN and VN should provide an alternative for a hard and lubricant coating for soft metals. In this study, CrAlN/VN multilayer coatings are deposited via magnetron sputtering to study the effect of the CrAlN/VN period thickness (\lambda) on the mechanical performance and tribological behavior at room temperature. At a proper period thickness, the coatings are of high hardness and low COF rendering low wear rate.

2. Experimental

2.1. Deposition of coatings

Six CrAlN/VN multilayer coatings (labeled as MA 1 though MA 6) with the same thickness ratios of CrAlN:VN = 1:2 were deposited
on polished YT15 cemented tungsten carbide (WC + 15 wt.% TiC + 6 wt.% Co) and silicon wafer (100) substrates in an in-line reactive magnetron sputtering system (PSU VH-200C, HOPE Vacuum Technology Co., Ltd., Taiwan). The sputtering targets were CrAl alloy (Cr: 70 at.% Al: 30 at.%) and pure V (99.99 wt.% purity), both of 152.4 mm in diameter. N came from the Ar/N₂ atmosphere controlled at 20 sccm/40 sccm. The coatings were prepared by two pulsed DC powers simultaneously. Through on-off and time control of target shutters, alternate deposition of VN or CrAlN layer was realized to form sequential CrAlVN coating with required thickness, finishing with VN at the top, the schematic of multilayer structure is shown in Fig. 1. CrAlN and VN monolayer coatings were also prepared and tested as reference. The designation and typical deposition conditions were listed in Table 1, multilayer coatings with varying period thickness labeled as MA 1 to MA 6.

2.2. Characterization

The chemical composition of the multilayer coatings was determined by field emission electron probe micro-analyzer (FE-EPMA, JXA-8500 F, JEOL, Japan) at 12 kV, 1.5 × 10⁻⁸ A. The crystalline structure analyses were conducted using grazing incidence X-ray diffraction (to avoid the influence from the substrate) (GIXRD, PANalytical-X’Pert PRO MPD) with Cu Kα radiation (40 kV, 30 mA, λ = 0.1541 nm) at a step size of 0.05° (0.3 s per step). The coating thickness was evaluated by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6701F, Japan) at 15 kV. The period thicknesses of the multilayer coatings were obtained by the total number of periods dividing the total coating thickness. Further characterizations for the multilayer structure were performed by transmission electron microscope (TEM, JEOL JEM-2100, Japan). 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 on each coating. The maximum indentation depth was limited to around 50 nm, which was less than one-tenth of the coating thickness. Ball-on-disk wear test was carried out to characterize the tribological performances. A tungsten carbide (WC) ball, 6 mm in diameter, was adopted as the counterpart. The tribo test was conducted at 24 °C and relative humidity of 65% with a normal load of 2 N for a sliding distance of 1000 meters. The sliding linear speed was set as 84 mm/s at radius of 4 mm. The COF was determined after 50 m running-in period to minimize the influence from surface topology [22]. The wear scars were examined by scanning electron microscopy (SEM, HITACHI S3400N) at 15 kV. The wear rate of the coating was determined based on the following equation [23]:

\[ W_R = \frac{t(3t^2 + 4b^2)2\pi}{6b^2n_5} \]  

where \( t \) is the depth of the wear track determined by a surface profilometer (Kosaka Surfcoorder ET3000), \( b \) 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 debris was then examined with X-ray Photoelectron Spectroscopy (XPS, Kratos, Britain) for chemical bonding using Al Kα (1486.71 eV) radiation (10 mA and 15 kV). Mixed Gauss/Lorentz peak deconvolutions (70% constrain) were used for peak fitting with Shirley-background reduction (i.e., XPS Peak 4.1 program).

3. Results and discussion

3.1. Physics/chemistry and microstructure

The thickness of monolayer CrAlN, VN coatings were 989 nm and 758 nm, respectively. The thickness of multilayer coatings were 842, 883, 928, 907, 903, 943 nm, respectively for MA 1 though MA 6; these values together with the respective period thickness are tabulated in Table 1. The mean chemical compositions of the multilayer coatings are 12.6% Cr–4.8% Al–34.2% V–45.0% N–3.4% O (in at.%). The average atomic ratios of (Cr + Al):V of each coating is around 1:1.97, very close to the designed 1:2.

<table>
<thead>
<tr>
<th>Sample designation*</th>
<th>CrAlN</th>
<th>VN</th>
<th>MA 1</th>
<th>MA 2</th>
<th>MA 3</th>
<th>MA 4</th>
<th>MA 5</th>
<th>MA 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Designed period thickness (nm)</td>
<td>–</td>
<td>–</td>
<td>3</td>
<td>6</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>30</td>
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<td>Period numbers</td>
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<td>–</td>
<td>300</td>
<td>150</td>
<td>90</td>
<td>60</td>
<td>45</td>
<td>30</td>
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<tr>
<td>CrAl target power density (W/cm²)</td>
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<td></td>
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<tr>
<td>V target power density (W/cm²)</td>
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<td></td>
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<tr>
<td>Base pressure (Pa)</td>
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<tr>
<td>Plasma etching</td>
<td>Argon plasma for 15 min at 0.4 Pa under substrate bias = 500V</td>
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<tr>
<td>Interlayer</td>
<td>70 nm thick CrAl interlayer for multilayer coatings</td>
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<td>Working pressure (Pa)</td>
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<tr>
<td>Ar/N₂ gas ratio</td>
<td>1:2</td>
<td></td>
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<tr>
<td>Total gas flow (sccm)</td>
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<td></td>
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<tr>
<td>RF substrate bias (V)</td>
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</table>

Coatings thickness (nm)

<table>
<thead>
<tr>
<th>Coatings thickness (nm)</th>
<th>989</th>
<th>758</th>
<th>842</th>
<th>883</th>
<th>928</th>
<th>907</th>
<th>903</th>
<th>943</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated period thickness (nm)</td>
<td>–</td>
<td>2.8</td>
<td>5.9</td>
<td>10.3</td>
<td>15.0</td>
<td>20.0</td>
<td>31.4</td>
<td></td>
</tr>
<tr>
<td>Lattice constant (nm)</td>
<td>0.4177</td>
<td>0.4139</td>
<td>0.4139</td>
<td>0.4140</td>
<td>0.4142</td>
<td>0.4142</td>
<td>0.4143</td>
<td>0.4140</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>20.2 ± 1.8</td>
<td>28.5 ± 2.5</td>
<td>25.1 ± 2.5</td>
<td>24.8 ± 3.1</td>
<td>28.1 ± 2.5</td>
<td>27.7 ± 2.1</td>
<td>32.4 ± 3.6</td>
<td>29.4 ± 2.2</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>298 ± 16</td>
<td>344 ± 23</td>
<td>309 ± 23</td>
<td>300 ± 14</td>
<td>341 ± 24</td>
<td>339 ± 22</td>
<td>375 ± 26</td>
<td>345 ± 24</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>0.32 ± 0.02</td>
<td>0.28 ± 0.02</td>
<td>0.27 ± 0.01</td>
<td>0.26 ± 0.01</td>
<td>0.32 ± 0.02</td>
<td>0.31 ± 0.02</td>
<td>0.31 ± 0.01</td>
<td>0.31 ± 0.02</td>
</tr>
</tbody>
</table>

* MA 1–6 are CrAlN/VN multilayer coatings.
The corrected values of lattice parameter (lattice constant: \(a_0\)) could be estimated from the Nelson–Riley function [25]:

\[
a = a_0 + K \frac{\cos^2 \theta}{\sin \theta}
\]

Eq. (4) represents a straight line between \(\cos^2 \theta/\sin \theta\) (X-axis) and \(a\) (Y-axis). The slope of the line gives the \(K\) and the intercept of this line on Y-axis gives the \(a_0\) and tabulated in Table 1. The lattice constants of monolayer CrAlN and VN are 0.4177 and 0.4139 nm, respectively; and there is about 1% mismatch. The \(a_0\) of CrAlN is larger than that of CrN (PDF card # 65-2899, \(a_{0\text{CrN}} = 0.4149\) signifying part of the doped Al acting as interstitial atom in CrN lattice structure. The lattice constants of multilayer coatings (0.4139, 0.4140, 0.4142, 0.4142, 0.4143, 0.4140 nm, respectively for MA 1 though MA 6) are very close to that of the monolayer VN (0.4139 nm). As the lattice constant of the multilayer coating is nothing but a weighted average of the constituents of the sublayers, dominating VN understandably results the multilayer coating’s lattice aligning toward that of the VN.

The TEM images and selected-area electron diffraction (SAED) pattern of the multilayer coating with period thickness of 20 nm (i.e., sample MA 5) are presented in Fig. 3; multilayer structure is observed from Fig. 3(a). The columnar grains are around 50 nm in width (cf., Fig. 3(b)). The thickness of one period measured from the image is about 20 nm, and the CrAlN/VN layer thickness ratio is about 1:2, in perfect agreement with design. In addition, the diffraction rings (cf., Fig. 3(b)) shown in SAED pattern have been identified as the B1 NaCl type.

### 3.2. Mechanical properties

Nanoindentation hardness \((H)\) and elastic modulus \((E)\) of the coatings are also tabulated in Table 1. The hardness and elastic modulus of multilayer coatings increase with period thickness varying from 3 nm to 20 nm; and at 20 nm, peaked at 32.4 GPa and 375 GPa, respectively. The plastic deformation resistance characteristics, or \(H^2/E^2\) [26], of CrAlN/VN multilayer coatings are plotted in Fig. 4, where \(E^2 = E[(1 - \nu^2)/\nu\text{Young's modulus,} \nu\text{is the Poisson ratio and} H\text{the hardness of the coating. The tendency between the plastic deformation resistance and period thickness is same with hardness; } H^2/E^2\text{peaked with 0.4 GPa at } A = 20\text{ nm. As comparison, the values of CrAlN and VN monolayer coatings are also shown in Fig. 4.}

In the case of “thick” layers: based on Chu and Barnett’s model [27], when the CrAlN/VN period thickness is 20 nm and higher (more than the interlayer width), dislocation gliding within individual layers determines the overall strength \((\sigma_{\text{tot}})\) of the multilayer coating, given by the scale average of the layer yield stresses \(\sigma_{\text{CrAlN}}\) and \(\sigma_{\text{VN}}\):

\[
\sigma_{\text{tot}} = \frac{I_{\text{CrAlN}}}{A} + \frac{I_{\text{VN}}}{A}
\]

where \(I_{\text{CrAlN}}\) and \(I_{\text{VN}}\) are the CrAlN and VN sublayer’s thickness. Thus, the lower-limit (required to move a pre-existing dislocation in a layer) and upper-limit (when there are not sufficient dislocations already exist, such that generation of dislocations is required) hardness enhancement for CrAlN/VN multilayer coatings can be achieved respectively as follows:

\[
\Delta H_{\text{lower-limit}} = \sigma_{\text{tot}} - \sigma_0
\]

\[
= \frac{2ab\cos \theta}{mA} \left[ \sigma_{\text{CrAlN}} \ln \left( \frac{I_{\text{CrAlN}}}{b\cos \theta} \right) + \sigma_{\text{VN}} \ln \left( \frac{I_{\text{VN}}}{b\cos \theta} \right) \right]
\]

\[
= 0.258 \times A^{-0.737} (\sigma_{\text{CrAlN}} + \sigma_{\text{VN}}) \cos \theta
\]
\[ \Delta H_{\text{Upper-limit}} = \sigma_{\text{tot}} - \sigma_0 = \frac{4\alpha b \cos \theta}{m \lambda} \times \left[ G_{\text{CrAlN}} \ln \left( \frac{k_{\text{CrAlN}}}{2b \cos \theta} \right) + G_{\text{VN}} \ln \left( \frac{k_{\text{VN}}}{2b \cos \theta} \right) \right] \]

\[ = 0.344 \times \lambda^{-0.672} (G_{\text{CrAlN}} + G_{\text{VN}}) \cos \theta \]  

(7)

where \(\sigma_0\) is the average stress required for dislocation slip in multilayer material, \(m\) is the Taylor factor, \(b\) is the magnitude of the dislocation Burgers vector, \(\alpha\) is \(\pi/4\) for screw dislocations and \((1 - \nu)\pi/4\) for edge dislocations, \(\theta\) is the smallest angle between the interface and the glide planes of crystal, set as \(45^\circ\) for multilayers [28]. \(G_{\text{CrAlN}}\) and \(G_{\text{VN}}\) are the shear moduli of CrAlN and VN layers (\(G = E/(2(1 + \nu))\), \(E\) is the elastic modulus and \(\nu\) is the Poisson’s ratio, 0.25 for CrAlN [29] and 0.279 for VN [30]). As the hardness of multilayer coating is inversely proportional to the layer thickness (i.e., \(t^2\)), MA 5 with \(\lambda = 20\) nm thus has higher hardness than that of MA 6 with \(\lambda = 30\) nm. Using Eqs. (6) and (7), for MA 5, the hardness enhancement is calculated as \(\Delta H_{\text{lower-limit}} = 5.1\) GPa and \(\Delta H_{\text{upper-limit}} = 8.2\) GPa. From the rule of mixture, the hardness of...
the multilayer coating should be 25.7 GPa \(= (H_{\text{CrAlN}} + 2 \times H_{\text{VN}})/3\).

For MA 5, however, the hardness is 32.4 GPa, or enhancement of 6.7 GPa, falling right in the calculated range of hardness enhancement limit (5.1–8.2 GPa).

In the case of “thinner” layers: as the period thickness decreases to 10 nm and 15 nm (MA 3 and MA 4 in which the CrAlN layer is 3.3 nm and 5 nm respectively), taken away the interface width, the CrAlN layer is too thin to contain dislocations. As such, the hardness is determined by the dislocation motion in VN layer (6.7 nm and 10 nm respectively), resulting similar hardness to VN coatings.

In the case of “extremely thin” layers: as the period thickness drops to 3 and 6 nm (MA 1 and MA 2 respectively), CrAlN sublayer is only 1 nm or 2 nm and the VN sublayer 2 or 4 nm, comparable with interface width; in addition, as CrAlN and VN have similar dislocation slipping systems with good miscibility, dislocation gliding.

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**Fig. 4.** \(H^2/E^2\) ratio of CrAlN, VN monolayer coatings and CrAlN/VN multilayer coatings with various period thicknesses.

**Fig. 5.** Wear rate of CrAlN, VN monolayer and CrAlN/VN multilayer coatings with different period thickness.

**Fig. 6.** Wear scars SEI and BEI images of multilayer coatings; (a) and (b) for the coating with period thickness of 3 nm, (c) and (d) for the coating with period thickness of 20 nm.
across interfaces thus determines the hardness, giving rise to the Rule of Mixture effect.

3.3. Tribological properties

Coefficients of friction of the as-deposited multilayer coatings together with the monolayer counterparts are shown in Table 1. COF of the monolayer CrAlN and VN is 0.32 and 0.28 respectively. The COF of their multilayer counterparts are not much different: 0.26–0.32. That is expected. Fig. 5 plots the wear rate of the multilayer coatings via ball-on-disk test. The multilayer coatings have wear rate from 1.1 to $6.7 \times 10^{-7}$ mm$^3$/Nm while that of the mono layer CrAlN and VN coatings are $1.8 \times 10^{-7}$ mm$^3$/Nm and $4.0 \times 10^{-7}$ mm$^3$/Nm, as inserted in Fig. 5. Fig. 6(a) and (b) is the wear scars of MA 1 (SEI and BEI images respectively). Fig. 6(c) and (d) is that of MA 5. Comparing a and c or b and d, MA 1’s wear scars have much more wear debris than that of MA 5 in the wear tracks. Obviously the wear rate was controlled by plastic deformation resistance, the coating with higher $H^3/E^2$ has lower wear rate as well as less wear debris. The lowest wear rate of $1.1 \times 10^{-7}$ mm$^3$/Nm occurs at $A = 20$ nm, consistent with the highest $H^3/E^2$ response. Fig. 7 (optical images) shows the wear scars of the tungsten carbide balls. For MA 1, the worn-out diameter is about 0.26 mm but for MA 5, the diameter is much larger or 0.29 mm. This agrees with the debris observation in the wear track: for softer coating (MA 1), more debris in the track and less wear in the ball while

![Fig. 7. Optical images of wear scars for tungsten carbide balls after tribo-test; (a) the ball for the coating with period thickness of 3 nm and (b) the ball for the coating with period thickness of 20 nm.](image-url)
for harder coating (MA 5), less debris in the track and more wear in the ball, which means the harder the coating is, more of the ball is worn resulting in a larger area of contact, and accordingly the contact pressure will decrease. A decrease in pressure should also result in lower wear rate of the coating.

The reasons of the self-lubricity lie in the formation of VO₃⁺ seen clearly in Fig. 8 that illustrates the XPS V 2p₃/2 spectra of the coatings and wear debris of λ = 20 nm. The binding energies of V₂O₅, V₂O₃, Al₂O₃ are 515.9 eV, 517.1 eV, 73.8 eV, and 74.3 eV, respectively [31]; and that of VN is 514.3 eV [32]. From Fig. 8(a) and (b), vanadium exists as VN, V₂O₃ and V₂O₅ in both coating and wear debris. Estimated from the fitted XPS peaks area, the content of VO₃⁺ (V₂O₅+V₂O₃) in unworn coatings is about 28%; similar phenomena can be found in the work of Franz et al. [12] and Glaser et al. [33]. As the multilayering ends with the VN sublayer on the top, and at room temperature, VN is typically oxidized several atomic layers following the so-called “low-temperature oxidation” mechanism [34]. Since XPS technique is only sensitive to a depth of about 10 nm [35], the VO₃⁺ percentage result thus only reflects the ratio within the XPS detectable depth (unworn or worn), not the VO₃⁺ bulk content of the coating. After tribo-test, the content of VO₃⁺ (V₂O₅+V₂O₃) increases from 28% (coating) to 35% (wear debris) due to tribo-oxidized VN. For the coatings with period thickness of 3 nm, it has lower plastic deformation resistance thus higher wear rate, more wear debris found in the wear track (see Fig. 6) which result in more VO₃⁺ Magnéli-phase slip planes and lower COF. Fig. 8(c) and (d) indicates that part of the aluminum element was oxidized from AlN to Al₂O₃ after ball-on-disk wear test. Since the Gibbs free energy of Al₂O₃ is −1582.0 kJ/mol which is lower than that of V₂O₅ (−1419.6 kJ/mol) and V₂O₃ (−1139.3 kJ/mol) [36], during tribo-test, Al can be oxidized preferentially thus partially retard the formation of vanadium oxides. This actually benefits retaining of hardness. In coatings with higher $H/d^{1/2}$ thus lower wear rate, less debris formed in the wear tracks (see Fig. 6), thus, result in less VO₃⁺ and higher COF.

4. Conclusions

Magnetron sputter formation of CrAlN/VN multilayer coatings from CrAlN and VN generates about 1% lattice mismatch in between the sublayers. The multilayer coatings are found self-lubricating with a coefficient of friction of 0.26 at room temperature because of formation of VO₃⁺. At period thickness of 20 nm, the coating exhibit nanoindentation hardness of 32.4 GPa, elastic modulus of 375 GPa and low wear rate of $1.1 \times 10^{-7} \text{mm}^3/Nm$ against cemented tungsten carbide.

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