Enhanced discharge and surface properties of (Ti,AlCr)N coatings by cleaning cathodic-arc chamber

Ying Konga, Xiubo Tian a,⁎, Chunzhi Gong a, Dmitriy A. Golosov b, Muqin Li c, Qinwen Tian a

a State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China
b Thin Film Research Laboratory, Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus
c School of Materials Science & Engineering, Jiamusi University, Jiamusi 154007, China

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ABSTRACT

In the PVD processes, the clearance of the chamber wall directly affects the microstructure and surface properties of the coatings. The (Ti,AlCr)N coatings are fabricated on M2 high-speed steel (HSS) and Si (100) by cathodic arc evaporation with the vacuum chamber cleaned or uncleared. With the chamber cleaned, the arc discharge was enhanced with a higher intensity of optical spectrum and the concentration of residual oxygen was decreased. The clearance of chamber wall altered the external behavior of powersupply and a largerinput power was achieved. The average substrate ion current was increased by 13.0% and a larger \( E_{bi} \) was observed implying increased densification of coatings. A thicker coating was obtained with less surface defects (macroparticles). Consequently the microstructure and surface properties of (Ti,AlCr)N coatings have been improved with higher hardness, lower friction coefficient and superior adhesion strength between the coatings and substrate.

1. Introduction

The increasing application of high-speed dry cutting requires more comprehensive hard coating systems with low friction and high thermal properties. TiAlN and CrAlN are widely used as protective coatings for cutting tools to improve their performance [1,2]. The TiAlN coating with supersaturated face-centered cubic structure can provide glorious hardness and thermal stability. In particular, the spinodal decomposition of c-TiAlN into nano-sized Ti- and Al-rich domains leads to the self-hardening effect under thermal load, which has been successfully applied to machining tools [3]. CrAlN is another prominent protective coating due to the outstanding tribological properties and resistance to oxidation. The appearance of dense oxide during exposure to air at elevated temperatures effectively retards growth kinetics of the oxide scale [4–6], which is responsible for exceptional oxidation resistance. Therefore, the (Ti,AlCr)N coatings have frequently attracted great attention, because of its potential to combine the self-hardening effect of TiAlN and outstanding oxidation resistance of CrAlN [7–8].

Among the reported deposition technologies, cathodic arc evaporation (CAE) is featured by several remarkable advantages over competitive physical vapor deposition techniques (e.g., sputtering and hollow cathode evaporation), giving rise to its importance and popularity in industrially-scaled synthesis of protective coatings [9–11]. Apart from high evaporation rates and degree of ionization of target materials, the CAE’s flexibility in terms of accessible material systems including metallic coatings, nitrides and oxides, represents an important key factor. During deposition processes, the microstructure and surface properties of the deposited films are determined by instrumental parameters including bias voltage [12], gas pressure [13], temperature [14], heat treatment [15], etc. In fact, these investigations have been widely reported in the numerous literatures. Besides the mentioned processing parameters, there are some other factors that cannot be ignored. Proper plasma cleaning (pre-deposition plasma treatment) effectively removes impurities from substrate surface and promotes good bonding, while excessive bombardment imparts more kinetic energy and causes peeling off due to residual stress [16]. Water vapor may stem from the residual atmosphere of the deposition chamber and the surroundings. They may be dissolved inside the deposited coatings, contaminate the surfaces and interfaces, and deteriorate the properties of coatings [17]. The position of the gas introduction into the chamber may affect the surface state and roughness of the substrates in the etching stage and the adhesion between the film and substrate. When gas is introduced near the arc source, the substrate surface is not rough relatively. In contrast, when gas is injected in the vicinity of the substrate, the substrate surface is rough [18]. The periodic variations in plasma density and fluxes of film-forming species may be produced by substrate rotation. This is utilized to modulate composition (e.g., nano-layer) and has drastic implications for the...
properties of coatings [19]. And, by adjusting the substrate position in the chamber, the lenticular-like fine grains, high density of micro twins, and better mechanical properties of coating can be achieved [20]. Similarly, the micro-blasting in the post treatment can induce residual compressive stresses to shift, which enhances tribological properties and the fracture resistance [21]. Of them, the effect of chamber-cleaning has been seldom reported although the chamber wall has to be cleaned regularly.

In this paper the (Ti,AlCr)N coatings were fabricated by cathodic arc evaporation (CAE) and two groups of experiments have been conducted. The first group of coating was deposited with the chamber cleaned and the second group was conducted with the chamber uncleaned. The substantial influence of chamber cleaning on the microstructure and mechanical properties of the coatings has been observed.

2. Experimental details

The (Ti,AlCr)N coatings were deposited on polished Si (100) and M2 high speed steel samples. The schematic diagram of the system used to deposit (Ti,AlCr)N coatings was shown in Fig. 1. The pure Ti (99.95%) and AlCr (99.95%) were utilized as targets. Substrates, (100)-oriented Si stripes and M2 high speed steel (Φ20mm × 4 mm) were ultrasonically cleaned in ethanol. After rinsing in distilled water and drying by hot air, the specimens were placed on the two-fold rotating carousel, which kept the rotation speed of 1.5rpm. After the chamber was evacuated below 3×10⁻³Pa and the temperature reached 400°C, the high pure (99.999%) Ar gas was introduced to keep a pressure of 1.5 Pa. The specimens were cleaned by arc-enhanced plasmas with pulsed bias voltage of 200 V for 45 min in order to remove the native oxide layers and contaminations from the substrates. After the above ion-etching process, the Ti and TiN interlayer were deposited for 15 min and 25 min respectively to improve the adhesion between the films and substrate. Then high pure (99.999%) nitrogen was added as reactive gas with constant pressure of 3 Pa. The Ti and AlCr targets were evaporated with arc current of 100 A. The cathodic arc deposition lasted 120 min for two groups of experiments with the chamber cleaned and uncleared. During the deposition, the carousel was biased with \( V_p = -30 \) V, pulsed frequency of 40 kHz, and duty cycle of \( D = 75\% \). Two groups of (Ti,AlCr)N coatings were deposited with target-substrate distance of 250 mm, 300 mm, 350 mm, 400 mm respectively. The detailed deposition parameters are listed in Table 1.

The substrate current was measured using a Tektronix digital oscilloscope via current sensor for the whole table assembly including the samples and holder. The optical emission signal was detected by a miniature fiber optic spectrometer AvaSpec-2048FT-4-DT, which was connected with the quartz fiber. The obtained emission signal ranged from 300 to 950 nm. The background spectrum was eliminated automatically in all recorded spectra. The structural analysis of coatings was performed by X-ray diffraction with Cu Kα radiation using a Bruker D8 diffractometer in Bragg/Brentano mode at 40mA and 40kV. The scanning angular (2θ) was ranged from 30° to 60° at a scanning speed of 4°/min. The cross-section scanning electron morphologies and the thickness of coatings were carried out by scanning electron microscope of Netherlands, FEI Quanta 200F. Secondary electron images (SEI) and backscattered electron images (BEI) were used to characterize the overall coatings thickness. Residual stress of the coatings was calculated based on the \( \cos \Psi \sin \Psi \) method, where \( \Psi \) is the angle between the normal to the coating surface and the diffracting lattice planes. The X-ray diffraction peak position shifts with the \( \Psi \) angle. The formula to calculate the residual stress is [22]:

Table 1
Deposition parameters for (Ti,AlCr)N coatings.

<table>
<thead>
<tr>
<th>Target-substrate distance (mm)</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ flow rate (sccm)</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base pressure (Pa)</td>
<td>( 3 \times 10^{-3} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti and AlCr target current (A)</td>
<td>100/100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate bias voltage (V)</td>
<td>-30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasma etching</td>
<td>Ar plasma for 45 min at 1.5 Pa under substrate bias</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>Deposition time (min)</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Surface resistance of chamber with different conditions.

<table>
<thead>
<tr>
<th>Plasma conditions</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>75.6</td>
</tr>
<tr>
<td>B</td>
<td>61.2</td>
</tr>
<tr>
<td>C</td>
<td>889.3</td>
</tr>
<tr>
<td>D</td>
<td>863.4</td>
</tr>
<tr>
<td>E</td>
<td>20.4</td>
</tr>
<tr>
<td>F</td>
<td>11.7</td>
</tr>
<tr>
<td>G</td>
<td>1023.0</td>
</tr>
<tr>
<td>H</td>
<td>1104.1</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of cathodic arc system.

Fig. 2. Resistance measurement at different sites of chamber wall.
Here, $S_2$ and $S_1$ are coating constants related to the Poisson’s ratio and elastic modulus (determined by nanoindentation, different for the coatings with different thickness). $\alpha$ is the angle related to the 20 diffraction angle and $\Psi = 0^\circ$, 15$^\circ$, 20$^\circ$, 25$^\circ$, 30$^\circ$, 35$^\circ$, 40$^\circ$ and 45$^\circ$.

The Vicker microhardness was measured by Zwick micro hardness tester using a pyramidal diamond indenter with an included angle of 136$^\circ$, 50 g indenting load for 20 s dwell time at 60 $\mu$m/s indentation rate. An average of three measurements was taken from five different positions in order to ensure the accuracy and repeatability of hardness. The friction coefficient was measured by ball-on-disk tester at room temperature and relative humidity of 50%. GCr15 ball of 6 mm in diameter with surface roughness Ra of 0.02 mm, 50 g was chosen as the counterpart and 5N load was applied. During the wear test, the relationship between friction coefficient and the sliding time was continuously recorded. The adhesion of the (Ti,Al,Cr)N coatings was evaluated by Rockwell indentation test using a Rockwell C diamond stylus (cone apex angle 120$^\circ$, tip radius $R = 0.2$ mm) at an applied load of 150 kg. Surface roughness was measured with an AFM system (Dimension Fastscan, Bruker, USA) at ambient conditions (25$^\circ$C, 35–40% Relative Humidity). For every sample the surface roughness (Ra) was inspected by the tapping mode in the areas of $2 \times 2 \mu$m$^2$.

### 3. Results and discussion

#### 3.1. Surface resistance of chamber wall

Fig. 2 presents the measurement of the surface resistance of the vacuum chamber at several positions. The surface resistance of...
An uncleaned chamber was increased by 33.4, 26.8, 403.2, 391.5, 4.3, 8.3, 464.1, 500.8 times than that of a cleaned one at the same site: A, B, C, D, E, F, G, H, as indicated in Table 2. It is due to the accumulated sediments on the wall, which affects the equivalent electrical conductivity.

Especially in the region on the carousel (e.g., the position E and F), the poor electrical conductivity at the uncleaned condition would give rise to the charging effect and the local electric field increased sharply [23], which led to the phenomenon of abnormal charge exchange, even marginal discharge.

Fig. 3 demonstrates the optical emission spectra of Ar II, Ti II and O2 I with chamber cleaned or uncleaned. The representative Ar II spectra lines (at 358.1, 396.7, 413.1 and 427.7 nm), Ti II spectra lines (at 307.2, 308.8, 316.2 and 319.2 nm) and O2 I spectra lines (at 435.1, 444.3, 459.6 and 468.2 nm) were recorded. Both the cleaned and uncleaned chamber wall did not change the position of any peak. However, the relative intensity of these peaks was different. It should be pointed that the spectrometer was reloaded for two groups of experiments (cleaned and uncleaned chamber). In order to confirm that the variation of emission intensity was not caused by reloading the instrument, the spectrum was recorded respectively as shown in Fig. 4(a) and (b). The error of spectral emission intensity was less than 10% (Fig. 4(c)) (five measurements were taken to ensure the accuracy and repeatability).

The IC/IU ratio of representative Ar II, Ti II and O2 I at different plasma conditions is depicted in Fig. 5. Here, IC and IU refer to the spectral intensity with the chamber cleaned and uncleaned respectively. The rise in spectra intensity for Ar II and Ti II with the chamber cleaned was easily observed (Fig. 3(a) and (b)) and the IC/IU for Ar II and Ti II was greater than 1. The population of Ar II and Ti II was related to the ionization of Ar atoms and Ti atoms in the discharge system. This implies the increase of ionization rate of the Ar and Ti [24]. On the contrary, the spectra intensity of O2 I decreased and the IC/IU for O2 I was less than 1, indicating the smaller number of oxygen atom/ions obtained from the clean chamber wall.

Oxygen may be attributed to the water and oxygen gas trapped in the chamber wall. The wall was deposited and contaminated by the plasma and neutrals from the vacuum arc and work gas. A loose and
thick contamination layer (particle, dust, etc.) may be formed on the chamber wall if the coating was deposited without cleaning the wall for a while. The water and oxygen in the air may be trapped in the contamination layer once the chamber door was open to unload or load the components to be treated. When the wall was heated and excited by the energetic particles including ions, electrons and some neutrals, the water and oxygen released and some of them may be excited and ionized by electrons. Thus the oxygen spectral emission intensity was high in the uncleaned chamber than in the cleaned chamber, which implied much richer residual oxygen.

Fig. 6 depicts the substrate current with the chamber cleaned and uncleaned. The average substrate current with cleaned chamber was increased by 13.0%, 5.6%, 4.1% and 1.9% with constant \( d_{TS} \) respectively. According to Child-Langmuir law \( J \propto n_e^2 \), where \( J \) is ion current, \( n_e \) is plasma density \([25,26]\), a higher plasma density would lead to a larger ion current. As shown in Fig. 3, a cleaned chamber produced higher plasma density and a higher current was achieved. It may produce a determinate effect on microstructure and surface properties of coatings \([27]\).

As illustrated in Fig. 7, with the cleaned chamber condition, the resistance of chamber was equal to zero \((R_1 = 0)\). In contrast, the equivalent resistance induced by contamination layer deposited on chamber wall was not zero with the chamber uncleaned (Fig. 7(a)). According to Ohm’s law applied in the arc \([28]\):

\[
U_f = U_{R0} + U_{R1} + U_a
\]

(2)

\[
I_{arc} = \frac{U_f}{R_0 + R_1 + R_{arc}} = \frac{U_a}{R_{arc}}
\]

(3)

(\text{where } U_f \text{ is the constant voltage of the power source, } U_a \text{ is the voltage across the arc, } U_{R0} \text{ is the voltage across the internal resistance of power source, } U_{R1} \text{ is the voltage across the contamination layer of chamber wall, } R_0 \text{ is the internal resistance of power source, } R_{arc} \text{ is the arc resistance, } R_1 \text{ is the resistance of chamber wall, and } I_{arc} \text{ is the current flowing through the entire circuit}). The maximum output current of the power supply was determined by Eq. (3):

\[
I_{\text{max}} = \frac{U_f}{R_0 + R_1}
\]

(4)

when the chamber was cleaned inferring that \( R_1 \) was equal to zero, the maximum current was equal to \( I_{\text{max}} = U_f/R_0 \) and external characteristics of the power supply corresponded to the curve 1. The curve 2 represented the external characteristics of the power supply with the chamber uncleaned \((R_1 \neq 0)\). And the maximum current was equal to \( I_{\text{max}} = U_f/(R_0 + R_1) \). The power supply ran at constant current mode. With the chamber uncleaned, the resistance of the contamination layer \((R_1)\) gave rise to a low equivalent arc voltage \((U_{arc})\) compared to original arc voltage \((U_{a1})\). The arc ran at a slightly lower voltage since the resistance of \( R_1 \) is not significant. This led to a lower input power to the arc system. Consequently the discharge was weakened and plasma density became lower as shown in Fig. 3. A reduced substrate current was observed (Fig. 6), which was not beneficial for the densification of deposited coatings.

3.2. Microstructure and properties of (Ti,AlCr)N coatings

Fig. 8 illustrates the X-ray diffractograms of the (Ti,AlCr)N coatings. As expected, the crystalline microstructure matches with the NaCl-B1 type structure (FCC) of aluminum chromium nitride and titanium nitride (JCPDS card #00-046-1200 and # 01-070-2942). For each scan, the change of diffraction intensity of cubic(c-) AlCrN (200) peak was neglected. However, the diffraction intensity of cubic(c-) AlCrN (111) peak increased distinctly with the chamber cleaned. The (Ti,AlCr)N coatings deposited with the chamber uncleaned (hereinafter referred to as U-(Ti,AlCr)N coatings) possessed lower crystallinity as indicated by the lower intensity. The lower mobility of adatoms on the surface, due to the less ion bombardment indicated by smaller substrate current (Fig. 6), would translate into weak crystallization and insufficient coalescence of grains and islands \([29]\).

With the chamber cleaned, arc discharge was enhanced and plasma density was higher near the substrate. Thus a larger substrate current was achieved. The intensive ion bombardment gave rise to the distortion of crystal lattice and the shift of diffraction peaks. A shift of diffraction peak to lower angles was related to the internal stress in the coatings \([30]\). According to Bragg equation, \( 1/d_{hkl} = (2/\lambda) \sin\theta \),
where dhkl, λ, and θ are the interplanar spacing of the (hkl) plane, wavelength of the X-ray, and half of the diffraction angle, respectively. The d value became larger when diffraction angle slightly shifted to the left. Table 3 demonstrates the residual stress of coatings with different chamber wall conditions. The compressive stress of C-(Ti,AlCr)N coatings was slightly larger than that of U-(Ti,AlCr)N coatings. It was attributed to the effect of atomic peening resulting from more ion bombardment, which may contribute to enhancement of mechanical

**Table 3**
Residual stress of coatings with different chamber wall conditions.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Residual stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d₁=250(mm)</td>
</tr>
<tr>
<td>Uncleaned</td>
<td>−4.41</td>
</tr>
<tr>
<td>Cleaned</td>
<td>−4.74</td>
</tr>
</tbody>
</table>
Fig. 9 shows the surface morphology of the (Ti,AlCr)N coatings. Larger size macroparticles were observed prominently on the surface of U-(Ti,AlCr)N coatings, whereas, the number of the defects decreased evidently on the surface of (Ti,AlCr)N coatings with the chamber cleaned (hereinafter referred to as C-(Ti,AlCr)N coatings).

Table 4 presents the elemental composition of the some macroparticles on the deposited surface and the contamination layer on the chamber wall.

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Ti</th>
<th>Al</th>
<th>Cr</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-(d_{r,g}=250) mm</td>
<td>46.73</td>
<td>19.78</td>
<td>25.71</td>
<td>7.78</td>
</tr>
<tr>
<td>C-(d_{r,g}=250) mm</td>
<td>47.01</td>
<td>18.27</td>
<td>26.51</td>
<td>8.21</td>
</tr>
<tr>
<td>U-(d_{r,g}=400) mm</td>
<td>46.02</td>
<td>19.84</td>
<td>26.28</td>
<td>7.86</td>
</tr>
<tr>
<td>C-(d_{r,g}=400) mm</td>
<td>45.95</td>
<td>19.63</td>
<td>25.92</td>
<td>8.50</td>
</tr>
<tr>
<td>Macroparticle</td>
<td>58.32</td>
<td>15.86</td>
<td>21.35</td>
<td>4.46</td>
</tr>
<tr>
<td>Contamination layer</td>
<td>48.74</td>
<td>20.97</td>
<td>21.45</td>
<td>8.84</td>
</tr>
</tbody>
</table>

Fig. 9 shows the surface morphology of the (Ti,AlCr)N coatings. Larger size macroparticles were observed prominently on the surface of U-(Ti,AlCr)N coatings, whereas, the number of the defects decreased evidently on the surface of (Ti,AlCr)N coatings with the chamber cleaned (hereinafter referred to as C-(Ti,AlCr)N coatings). Table 4 presents the elemental composition of the some macroparticles on the deposited surface and the contamination layer on the chamber wall in Fig. 9(e) and (f). They had the same elements (including Ti,Al,Cr and N) although the concentration was slightly different. Especially more defects were observed with the chamber uncleaned, inferring they may originate from cathodic arc as well as dirty chamber wall [31]. These particles and contaminations easily broke away due to the mechanical micro-vibration, the collision between electrons, energetic neutrals and properties to some extent.
chamber wall as illustrated in Fig. 10. Besides, the poor electrical conductivity of chamber wall (Table 2) might result in the charging effect, electrostatic repulsion and even local micro-arc, which produced more peeling off of contaminations. The macroparticles from the wall floated in the chamber in conjunction with those from the cathodic arc. The contaminations were loosely adhered on the surface due to the weakened bombardment effect with chamber uncleaned.

These particles may be charged with electrons, which were repelled far from substrate surface when the negative bias is applied [32–34]. And intensive ion bombardment tended to get rid of the macroparticles on the surface [35–37]. With the chamber cleaned a higher plasma

Fig. 10. Illustration of peeling off of contaminations from chamber wall.

Fig. 11. Cross-sectional morphology of the coatings deposited at different conditions: (a) U-\(d_{T-S}\) = 250 mm, (b) C-\(d_{T-S}\) = 250 mm, (c) U-\(d_{T-S}\) = 400 mm, (d) C-\(d_{T-S}\) = 400 mm.

Fig. 12. Thickness of coatings \(D\), and \(E_{bi}\) at different conditions: (a) Coating thickness \(D\), (b) \(E_{bi}\).
Fig. 11 demonstrates the cross-sectional micrographs of (Ti,AlCr)N coatings deposited. All of coatings presented the compact structures with columnar growth. The C-(Ti,AlCr)N coatings have a higher deposition rate as shown in Fig. 12(a). As mentioned in Fig. 6, the substrate ion current increased after the chamber is cleaned. A higher more ionic flux exerted a positive effect on the higher deposition rate. In fact the high density plasma may be also related to a larger input power to cathodic arc. A slight increase of arc voltage was induced as illustrated in Fig. 7. This led to more evaporation of target materials. An increased deposition rate was achieved due to high density of ions and atoms.

Fig. 12 summaries the changes in the coating thickness (D) and Ebi as a function of target-substrate distance. The Ebi refers to the ratio of substrate ion current to thickness, which is frequently used to evaluate the compactness of the coating [38]. The substrate current is proportional to the number of incident ions depending on plasma density around samples. A larger Ebi value implies that the coating may be bombarded by more energetic ions and denser film may be produced. As depicted in Fig. 12(b), the cleaned chamber gave rise to an increased Ebi suggesting that the more compact structure of C-(Ti,AlCr)N coatings was induced although the deposition rate increased evidently.

Fig. 13 exhibits the vickers micro-hardness of the (Ti,AlCr)N coatings. The C-(Ti,AlCr)N coatings has a relatively higher hardness compared to U-(Ti,AlCr)N coatings with the same dTS. It may be attributed to several factors. A higher hardness is related to larger residual stress [39–40] of C-(Ti,AlCr)N coatings, which is supported by XRD results as shown in Fig. 8. Another hardening factor is densification effect of micro-structure [41]. More blocks are allowed to create at grain boundaries, thus inducing the pinning effect, inhibiting the migration and strengthening the influence of dislocation blocking against the grain boundary [42]. The Ebi value of C-(Ti,AlCr)N coatings (Fig. 12) increases to some extent, which indicates that the densification of coatings is improved than that of the U-(Ti,AlCr)N coatings. Therefore, the C-(Ti,AlCr)N coatings hardness is enhanced dramatically. Besides, the growth of C-(Ti,AlCr)N coatings demonstrates a stronger diffraction intensity of c(111) plane (Fig. 8). The effect of the coherency strain (c-plane) may contribute to enhancement of hardness [43]. At the dTS of 250 mm, the hardness of C-(Ti,AlCr)N coating was evidently higher than that of U-(Ti,AlCr)N coating. It may be attributed to the similar Ebi value of C-(Ti,AlCr)N coatings (Fig. 12) and the density of incident ions depending on plasma density around samples. A larger Ebi value implies that the coating may be bombarded by more energetic ions and denser film may be produced. As depicted in Fig. 12(b), the cleaned chamber gave rise to an increased Ebi suggesting that the more compact structure of C-(Ti,AlCr)N coatings was induced although the deposition rate increased evidently.

Table 5

<table>
<thead>
<tr>
<th>Condition</th>
<th>Ra (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dTS = 250 mm</td>
<td>dTS = 300 mm</td>
</tr>
<tr>
<td>Uncleaned</td>
<td>88.3</td>
</tr>
<tr>
<td>Cleaned</td>
<td>86.7</td>
</tr>
</tbody>
</table>

density gave rise to more effect of repelling and bombardment to the macroparticles. Consequently fewer defects were observed on the surface compared to those with the chamber uncleaned, due to synergistic effect of less contamination and higher plasma density.

Fig. 14 shows the friction coefficient (COF) of the (Ti,AlCr)N coatings. The gradual evolution of COF was detected during the full test. The friction behavior of each sample underwent a pre-grinding stage about 200 s, which was quite complex and mainly related to the surface conditions. Then the coefficients were approximately kept stable for the rest of whole sliding time. The COF of U-(Ti,AlCr)N coatings was slightly larger than that of C-(Ti,AlCr)N coatings, which can be associated with the roughness of surface [47,48]. Table 5 illustrates the roughness (Ra) of the produced coatings. The Ra values of U-(Ti,AlCr)N coatings was slightly larger than that of C-(Ti,AlCr)N coatings, which was related to the existence of more macroparticles (Fig. 9) on the surface of U-(Ti,AlCr)N coatings. Higher roughness reduced the actual contact area between the ball and coating, which resulted in the load only focusing on the contact areas and then enhanced the friction.
In addition, the decreased substrate current of U-(Ti,AlCr)N coatings implied weak bombardment effect leading to less compactness of the coatings.

Fig. 15(a) and (b) show the wear of the friction counterparts. The diameter of wear scar of the ball against C-(Ti,AlCr)N coatings was larger than that against U-(Ti,AlCr)N coatings. The ball sliding on harder coating exhibited larger wear area demonstrating higher wear rate [50]. When sliding, the harder coatings (C-(Ti,AlCr)N) could lead to a considerable wear volume of the balls. Fig. 15(c) and (d) present the typical image and EDS elemental analysis of wear track surface.

Table 6 presents the elements in the wear track surfaces of different coatings. The Fe element was detected on the coatings (which were not broken through at a closer look). In addition, no violent fluctuations of friction coefficient were found (Fig. 14), indicating that the debris was related to the counterpart balls [51]. In fact the temperature at the interface between the ball and coatings was elevated during the sliding process, which would cause oxidation [52]. (Oxygen was detected on worn surfaces as shown in Table 6). The content of Fe (at. %) on the wear track surface of U-(Ti,AlCr)N coatings is slightly lower than that on C-(Ti,AlCr)N coatings. For the steel ball, the debris was generated on the nitride coating, which could be entrapped into the rubbing surface, resulting in the formation of scratch and consequently the wear mechanism was mainly abrasive wear [53]. In abrasion wear, the steel ball and the coating surface would rub each other resulting in plastic deformation, flow and microcutting, etc. Additionally, the iron oxide layer from steel ball also adhered to the coating surface due to higher hardness of nitride [54]. With the chamber cleaned, the hardness of C-(Ti,AlCr)N coating was enhanced, inducing more materials from counterpart ball were abraded down and a higher Fe concentration was found on the wear track surface of coating.

Fig. 16 depicts the surface morphology of samples after indentation by using TH320 Rockwell hardness tester (load of 1470N). In reference to standard drawing VDI 3198 (the standard damage pictures serve to classify adhesion into six classes HF1-HF6 [55]), the adhesion strength between the C-(Ti,AlCr)N coatings and substrate was relatively high. The spallation of U-(Ti,AlCr)N coating at \( d_{T-S} = 250 \text{ mm} \) was observed clearly and the adhesion strength seemed to be the poorest, which can be identified as class HF5. The C-(Ti,AlCr)N coating at \( d_{T-S} = 250 \text{ mm} \) showed only a few cracks around the indentation referred to as class HF2. The poor adhesion of coatings may be attributed to a higher stress stemming from larger thickness and excessively intensive bombardment. In contrast, the indentation for the C-(Ti,AlCr)N coating at \( d_{T-S} = 300 \text{ mm} \) was clear and smooth with no spherical cracks and dew points. The adhesion may be identified as HF1, which is distinctly superior to that of U-(Ti,AlCr)N coating.

With the chamber cleaned, less water and oxygen trapped in the contamination layer would release and be excited and/or ionized as shown in Fig. 3. A better interface is expected. A cleaned chamber may lead to a higher plasma density and an effective ion-sputtering of native oxides and impurities, which gives rise to an increase in the coating coefficient of the coating [49]. In addition, the decreased substrate current of U-(Ti,AlCr)N coatings implied weak bombardment effect leading to less compactness of the coatings.
Fig. 16. The indentation morphology of the (Ti,AlCr)N coatings at different conditions:
(a) U-d_f,s = 250 mm, (b) C-d_f,s = 250 mm, (c) U-d_f,s = 300 mm, (d) C-d_f,s = 300 mm, (e) U-d_f,s = 350 mm, (f) C-d_f,s = 350 mm, (g) U-d_f,s = 400 mm, (h) C-d_f,s = 400 mm.
adhesion [56]. Grain refinement induced by intensive ion bombardment may increase crack propagation resistance [57], which could re-strengthen the coating peelage.

4. Conclusion

The (Ti,Al,Cr)N coatings have been deposited by the cathodic arc technique with the chamber cleaned and uncleaned. The chamber cleaning has a distinct effect on the substrate ion current, plasma emission spectrum, microstructure, surface defects and mechanical properties of coatings. With the chamber cleaned, the equivalent resistance of chamber wall was significantly reduced. The higher emission intensity of O2I indicated the reduced content of residual gas. Cleaning of chamber wall is critical. The higher emission intensity of O2I indicated the reduced content of residual gas. Cleaning of chamber wall is critical. The higher emission intensity of O2I indicated the reduced content of residual gas. Cleaning of chamber wall is critical.

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