Ti- and Cr-based hard coatings obtained at low temperatures by unbalanced magnetron sputtering

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Abstract. We prepared a set of Ti- and Cr-based ternary and quaternary hard coatings at low deposition temperatures (< 200 °C) by closed-field unbalanced magnetron sputtering in a gas mixture of Ar + N2. The morphological, structural and mechanical properties of the coatings were characterized by means of atomic force microscopy, scanning electron microscopy, X-ray photoelectron spectrometry, a micro-scratch tester and a nanoindentation tester. The results of the analyses performed revealed that the surface of the deposited ternary Ti-Al-N coatings was rougher than that of the CrTiAlN coatings. The metallic elements in the coatings react with nitrogen to form CrN, TiN and AlN nitride phases, as no Cr2N phase was detected in the Cr-based coatings. The optimized quaternary coating demonstrated mechanical properties superior to those of the ternary ones in terms of hardness; adherence strength of 32 GPa and elastic modulus of 418 GPa were measured for the multicomponent coating of composition Cr0.68Ti0.19Al0.13N.

1. Introduction
Hard coatings based on Ti and Cr nitrides are widely used as protective coatings. A large number of studies have been reported on the deposition and properties of CrTiN, TiAlN and CrAlN coatings produced by various PVD techniques. The TiAlN coatings have been developed as an alternative to TiN, because of their higher oxidation resistance, enhanced hardness and higher corrosion resistance [1-5]. The CrAlN coatings have exhibited superior mechanical properties and oxidation resistance in comparison to the traditional binary TiN and CrN coatings [6, 7] and have been successfully used in the industry. Films based on the Ti-Cr-N system have also been deposited using a variety of deposition methods in order to improve their wear and oxidation resistance [8-10]. Further improvements in

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nitride coatings have been found to result in better performance compared to that of ternary films. The Ti–Al–Cr–N system offers a high variability of composition, ranging from Cr-rich to Al-rich [11-13] coatings. These films have demonstrated improved hardness and thermal stability, oxidation resistance and exhibited lower friction and wear. Among the PVD coating technologies, the closed-field unbalanced magnetron sputtering is an exceptionally versatile technique for the deposition of high-quality, well-adhered films. The main advantages of this technique are as follows: possibility for deposition at low temperatures, including room temperature, use of non-toxic working gases, a high degree of smoothness, uniformity and density of the deposited coatings.

The present study focuses on the investigation of the Ti- and Cr-based coatings obtained by a closed-field unbalanced magnetron sputtering technique. The goal of this work is to establish optimal technological regimes which provide stable mechanical properties of the system “substrate - coating”.

2. Experimental details

2.1. Deposition of Ti and Cr-based coatings

The UDP850 (CFUBMS) closed-field unbalanced magnetron sputtering system was equipped with four rectangular cathodes of high-purity (99.99%) Cr, Ti and two Al targets operated in an unbalanced magnetron mode. A schematic illustration of the sputtering system is shown in figure 1 (a). The closed magnetic field coupling results in a high degree of ionization and biased current density. The coatings were deposited onto substrates of high-speed steel (EN: 1.3343), stainless steel (EN: 1.4436) and carbon tool steel with low thermal resistance (EN: CT105). Prior to deposition, the substrates were cleaned in an ultrasonic bath for five minutes at a temperature of 65 °C using commercial cleaning solution to remove oils, residues and protection against corrosion. The substrates were then rinsed in distilled water for two minutes, followed by ultrasonic cleaning in hot isopropanol for five minutes and drying. Generally, the ultrasonically cleaned metal substrates have a thin top oxide layer, which affects the adhesion. Thus, after the wet chemical cleaning, the substrates were loaded in the deposition chamber and the system was pumped down to a base pressure of less than 2.5×10⁻³ Pa. In order to remove the top oxide layer, the substrates were plasma-cleaned in argon ambient (1.7×10⁻¹ Pa) for 30 minutes at a negative pulsed substrate bias voltage of 500 V and a frequency of 250 kHz.

In all deposition processes, the substrates were rotated axially at a speed of 5 rpm in order to obtain a homogenous film composition. The distance between the substrates and the targets was kept at 150 mm. All the experiments were conducted without additional substrate heating at a bias voltage of −70 V and a frequency of 150 kHz in a DC work mode for of the Ti and Cr cathodes, and a pulsed mode for the Al cathodes. A mixture of argon and nitrogen gases was introduced into the chamber during the deposition process at a fixed Ar flow-rate of 25 sccm. A nitrogen level of 95–50% was provided with the help of a plasma optical emission monitor with a feedback control system (figure 1 (b)).

![Figure 1. Cross-sectional schematic drawing of the CFUBMS sputtering system - (a) and the optical emission control scheme - (b).](image-url)
Three series of experiments were performed for deposition of Ti-based and Cr-based ternary and quaternary coatings using Cr, Ti and Al as the sputtering targets. Pure argon (99.9999%) and nitrogen (99.9999%) were used as the sputtering and reactive gases, respectively. The relative concentration of metals (Cr, Ti and Al) was adjusted by the sputtering power applied to each metallic target. The additional details of deposition conditions used in this study are presented in table 1. In the first series, TiAlN coatings were deposited using Ti as the adhesive layer and TiN as an interlayer. In the second series, CrTiN coatings were deposited using Cr and CrN as the adhesive layer and interlayer respectively. In the third series, Cr-Ti-Al-N coatings were deposited using Ti (or Cr) as the adhesive layer and TiN (or CrN) as an interlayer. Following these two layers, a compositionally-graded Cr-Ti-Al-N top layer was deposited.

2.2. Study of coating properties

The mechanical properties were investigated using Compact Platform CPX (MHT/NHT) CSM Instruments equipment, which includes a nanoindentation module (NHT), a micro-scratch module (MST) and an optical video microscope with a CCD camera, installed together on the same platform. Nanoindentation was performed by a triangular diamond Berkovich pyramid in the loading interval of 10 – 200 mN. The nanohardness (H) and elastic modulus (E) were calculated from nanoindentation load-displacement data at a periodic loading and unloading of the samples at a successively increasing load using an Oliver & Pharr method implemented by software. The adhesion strength of the coatings to the substrate material and the friction coefficient were evaluated using an MST equipped with a spherical Rockwell indenter with a radius of 200 μm under the following test conditions: progressively increasing pressing force in the range of 1 – 30 N; loading rate 0.5 N/min; indenter movement speed 0.02 mm/min; and acoustic emission detector sensitivity 9. The nature of the resulting damages was assessed by observations with the optical video microscope equipped with a CCD camera.

The morphology and roughness of the deposited coatings were studied using a NanoScope VAFM (Bruker Inc.) atomic force microscope in tapping mode in air. Silicon cantilevers were used with reflective aluminium coating of 30-nm thickness (Tap 300Al-G Budget Sensors, Innovative Solutions Ltd, Bulgaria). The characteristics of the cantilevers were as follows: spring constant from 1.5 to 15 N/m, resonance frequency 150 ± 75 kHz and tip curvature radius of less than 10 nm. The scanning rate was set at 1 Hz. The roughness analysis yields the value $R_m$, which is an arithmetic average of the absolute values $Z_i$ of the surface height deviations measured from the mean plane, while the image $R_q$ is the root-mean-square average of the height deviations taken from the mean image data plane.

Surface observation and composition analysis were performed on a JEOL JSM 6390 electron microscope equipped with an INCA Oxford EDS energy dispersive detector. Surface images were also obtained in secondary electrons (morphology contrast) and back-scattered electrons (density contrast).

The coatings’ chemical bonding was studied by X-ray photoelectron spectrometry (XPS) using a Kratos AXIS Supra photoelectron spectrometer with a monochromatic Al Kα source with energy 1486.6 eV. The base pressure in the analysis chamber was 5×10⁻⁸ Pa. The binding energies were corrected relative to the C1s peak at 285.0 eV. The elemental concentration was derived on the basis of the core level peak areas, corrected by the corresponding values of the relative sensitivity factor.

3. Results and discussion

3.1. Surface morphology and roughness

Several scans were performed by the AFM in tapping mode over different areas. The AFM data revealed that all the coatings exhibited a densely-packed structure [14] consisting of well-separated grains with apparently spherical form and predominantly equal sizes. The surface morphology of TiAlN and CrTiAlN coatings with different Ti and Al content are shown in figure 2 and figure 3. It is visible that the TiAlN coating surface is rougher than that of the CrTiAlN coating. The average roughness ($R_a$) and the root-mean-square ($R_q$) surface roughness obtained on a scanned area of
10 µm×10 µm were as follows: for the ternary coating $R_a = 29.9$ nm and $R_q = 38.8$ nm; for the quaternary coating $R_a = 16.4$ nm and $R_q = 22.0$ nm.

**Figure 2.** Surface topography of the TiAlN coating (SS substrate) obtained by AFM: a) 2D image; b) 3D image.

**Figure 3.** Surface topography of the CrTiAlN coating (SS substrate) obtained by AFM: a) 2D image; b) 3D image.

3.2. Mechanical properties

3.2.1. Nanohardness The mechanical parameters of the developed coatings were investigated in dependence on the nitrogen flow and cathode current. The nanohardness $(H)$ and elastic modulus $(E)$ were calculated from nanoindentation load-displacement data at a periodic loading and unloading of the samples at a successively increasing load using an Oliver & Pharr method. To eliminate the influence of the substrate on the measurement, a load of 10 mN or 15 mN was applied, which corresponded to a maximum indentation depth of less than 10% of the coating thickness. The results showed that, among the technological parameters quoted, the presence of nitrogen affected most strongly the mechanical properties of the coatings. Table 1 lists the mechanical properties of the ternary and quaternary coatings, the latter exhibiting better mechanical properties in terms of hardness and adherence strength.
All the coatings demonstrated hardness higher than that of the TiN and CrN coatings (25 GPa and 18 GPa). We attribute the improved hardness of the CrTiAlN coating to the hardening of the solid solution by the addition of Ti and Al elements in the CrN crystals. The nanohardness obtained is significantly higher than those reported in [15, 16] and agrees with that obtained in [17].

3.2.2. Adhesion Three scratches on the coated HSS substrates for each sample were carried out in order to determine the adhesion and coating toughness. During the tests, the load was increased progressively in linear mode from 1 N to 30 N at scratch lengths of 1 mm and 3 mm and constant scratch speeds of 0.02 mm/min and 0.05 mm/min. The critical load \( L_c \) values were determined after the test by optical microscopy observation of the damages formed in the scratch tracks and from the recorded acoustic emission (AE) and friction force \( F_t \) signals. The critical loads \( L_c1 \) and \( L_c2 \) indicate the appearance of the first cohesive and adhesive cracks, respectively [16]. Figure 4 shows scratch graphs of the TiCrAlN/HSS coating and the optical micrographs of the main parts of the scratch track with cracks at different locations. We found that increasing the scratch length and the normal load results in changes in the values of the friction force and acoustic emission. Very slight semi-circular cracks were observed at a normal load of about 5 N (figure 4f). The first critical load was registered at \( F_s = 12.5 \text{ N} \) (figure 4f), and the second one, at \( F_s = 23 \text{ N} \) (figure 4g). A distortion of the line of the friction force and the acoustic emission was observed at a higher normal load \( F_s = 23 \text{ N} \).

As a result of the tests carried out, we established that the critical loads \( L_c1 \) and \( L_c2 \) are observed for the Ti-based coatings, while the Cr-based coatings exhibit very good adhesion properties in the loading range 1 – 30 N. The coefficient of friction of the coatings against a diamond indenter was measured to be \( \mu = 0.1 - 0.2 \). The best adhesion result without any visible damages within the loading range of 1 – 30 N was exhibited by the CrTiAlN coating (table 1).

### Table 1. Deposition conditions and mechanical properties of deposited coatings.

| Coating   | OEM [%] | Cathode current current \( I_{Cr}/I_{Al} \) [A] | Substrate temperature \( T \) [°C] | Thickness [μm] | Hardness \( H \) [GPa] | Elastic modulus \( E \) [GPa] | Coefficient of friction \( \mu \) | Critical load \( L_c1 \) [N] |
|-----------|---------|-----------------------------------------------|-----------------------------------|----------------|-----------------|-----------------|-----------------|-----------------|
| TiAlN     | 45      | 5/0/3                                         | 130                               | 2.0            | 29              | 365             | 0.1             | 16.5            |
| CrTiN     | 60      | 8/5/0                                         | 134                               | 1.5            | 26              | 331             | 0.2             | 24.5            |
| TiCrAlN   | 50      | 8/5/3                                         | 155                               | 2.5            | 28              | 358             | 0.2             | 21.0            |
| CrTiAlN   | 60      | 8/5/3                                         | 147                               | 2.0            | 32              | 418             | 0.1             | > 30            |

3.3. Composition and chemical bonding analysis

The chemical bonding structure of the coating samples was investigated by XPS. The TiAlN, CrTiN and CrTiAlN coatings presented similar binding-energy spectra. Typical spectra of TiAlN coating in Ti 2p, Al 2p and N 1s energy ranges are shown in figure 5.

It is seen that the peak associated with Ti (figure 5a) consists of two peaks centered at 457.0 eV and 462.1 eV. These peaks originate from Ti 2p3/2 and Ti 2p1/2 electrons in titanium oxynitride. Figure 5(b) shows the XPS spectra for the corresponding Al2p levels. The contribution in figure 5(b) with a maximum binding energy at 73.7 eV is attributed to the Al-N chemical bonding state within the coating. The fact that the N1s spectrum after etching shows only one peak with a binding energy of approximately 396.3 eV (figure 5c) is attributed to the presence of nitride films (TiN and AlN) [18, 19]. A similar bonding status of Ti2p, Al2p and N 1s and typical XPS spectra were obtained for CrTiN and CrTiAlN samples. The weak Ti2p and Al2p XPS spectra and the stronger spectra of N1s and Cr2p are plotted in figure 6. The spectrum of N1s at 396.5 eV can be related to CrN. In the Cr2p spectrum,
Figure 4. Typical scratch graphs on the Ti- (upper figure) and Cr-based multicomponent coatings and optical micrographs (e, f and g) of the main parts of scratch track with cracks at different locations: a) normal load; b) acoustic emission; c) friction force; d) friction coefficient.

Figure 5. XPS spectra of (a) Ti 2p, (b) Al 2p and (c) N 1s of a TiAlN sample before and after sputter etching in Ar.
the peaks centered at 575.1 eV and 585 eV can be attributed to Cr-N bonds. Peaks pertaining to free Cr metal and Cr2N cannot be observed [21], indicating that the bonding state of chromium is in the form of CrN.

The coatings’ composition was determined by EDS and XPS analyses. The elemental concentrations of the coatings determined by EDS (table 2) were also compared with the results obtained by XPS. The XPS analysis was in good agreement with the EDS results (within ±2%).

**Table 2.** Composition and chemical formulae of the coatings investigated.

| Formulae                  | EDS analysis results [in at %] |
|---------------------------|--------------------------------|
| Cr<sub>x</sub>Ti<sub>y</sub>Al<sub>z</sub>N | Cr  Ti  Al  N  |
| Ti<sub>0.36</sub>Al<sub>0.64</sub>N | 0  9.54  16.59  45.43 |
| Cr<sub>0.7</sub>Ti<sub>0.3</sub>N | 44.85  19.09  0  30.13 |
| Cr<sub>0.68</sub>Ti<sub>0.19</sub>Al<sub>0.13</sub>N | 30.33  86.8  56.9  50.72 |

4. Conclusion

The experimental results demonstrated that proper addition of either Ti and Al into the CrN structure leads to an improvement in the mechanical properties of the coatings. No significant differences were found between the mechanical properties of the coatings obtained on HSS and carbon tool steel substrates. However, the Cr-based coatings demonstrated a lower average surface roughness than the Ti-based coatings. The optimized quaternary Cr-Ti-Al-N coating exhibited enhanced mechanical properties compared to the ternary Cr-Ti-N and Ti-Al-N ones in terms of hardness and adherence strength. The maximum nanohardness of 32 GPa and elastic modulus of 418 GPa for the multicomponent coating were measured for the composition Cr<sub>0.68</sub>Ti<sub>0.19</sub>Al<sub>0.13</sub>N. The results showed that among the technological parameters mentioned, the presence of nitrogen was the factor affecting the most strongly the mechanical properties of the coatings.

4. References

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