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Effect of the heat treatment on mechanical and structural properties of CrTiAlN coatings deposited at low temperature

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The present article investigates the mechanical properties and microstructure of the CrTiAlN thin coatings obtained at a low deposition temperature (150°C) using Closed Field Unbalanced Magnetron Sputtering (CFUBMS) technique onto different substrates. In order to determine the effect of heat treatment on mechanical and structural properties, the as-deposited CrTiAlN coatings were annealed in an argon atmosphere and air at different temperatures (400-800°C) for 2 hours. The alteration of the morphology, microstructure, chemical composition, hardness and adhesion strength after the treatment was analysed by atomic force microscopy (AFM), scanning electron microscopy (SEM) complemented with an energy dispersive x-ray spectroscopy analysis, X-ray photoelectron spectroscopy (XPS), a Nanoindentation Tester and a Micro Scratch Tester. After an annealing to the temperature of 600°C the coatings demonstrated higher hardness and elastic modulus of 29 ± 2 GPa and 365 ± 20 GPa, respectively. Further increase of the treatment temperature caused decrease of the coating hardness and elastic modulus and rise of the surface roughness and coefficient of friction.

Keywords: UBMS, hard coatings, CrTiAlN, thermal resistivity

INTRODUCTION

Thin films deposition has undergone huge advance in the last decades and it is now possible to obtain multilayered, functionally gradient, and nanocomposite coatings that have very good properties, such as high hardness, good adhesion and high wear- and oxidation resistance. Thermal stability of the coatings at high temperatures is a concern not only for applications in hot environments, but also in cutting and drilling operations, where locally temperatures of up to 800 ºC can be reached.

A wide range of PVD hard coatings are now available for a variety of applications. TiN is the first generation of PVD hard coating (about 24 GPa) and is still being used as protective hard coatings for bearings, gears, cutting and forming tools. However, the fracture toughness and low oxidation resistance (< 550 ºC) of the TiN coatings are not satisfactory for many engineering applications [1,2]. In the advance of hard coating development, TiAlN has been successfully commercialised particularly for high-speed cutting because of its significantly improved oxidation resistance (>700 ºC) and hardness over TiN [3-6].

Nevertheless, the oxidation resistance at elevated temperatures of the Ti-based coatings is limited although it has been improved with aluminium incorporation. These drawbacks of the Ti-based coatings have strongly limited their practical applications. Similar to TiN, chromium nitride, CrTiN and AlCrN coatings have been successfully applied to the metal forming and plastic moulding dies and wear components, which is known to be superior to TiN in wear resistance, friction behaviour, and toughness [7-9]. Further improvements in nitride coatings have been found to have promising performance compared to that of ternary films. Cr–Ti-Al–N system offers a high variability ranging from Cr rich to Al rich [10-13] coatings with improved hardness and thermal stability, oxidation and wear resistance and lower coefficient of friction.

The present article investigates the effect of heat treatment in air and argon environment on mechanical properties, microstructure and phase composition of CrTiAlN coatings with a small amount of Al, obtained at a low deposition temperature.

EXPERIMENTAL DETAILS

Coatings deposition conditions

Cr-Al-Ti-N coatings with different thickness

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were prepared using a Teer Coatings UDP 850 closed-field unbalanced magnetron sputtering (CFUBMS) system. The system was equipped with four unbalanced magnetrons uniformly arranged at 90° intervals around the vertical stainless steel vacuum chamber. Each magnetron was fitted with a target: Cr, Ti and two Al. The coatings were deposited onto substrates of high-speed steel (EN: 1.3343), stainless steel (EN: 1.4436) and carbon tool steel (EN: CT105) with low temperature resistance (≤ 200°C). The high-speed steel (HSS) and carbon tool steel substrates were preliminary hardened. The substrate holder comprised a rotating vertical rod, supporting a pair of horizontal plates on which the substrates were fixed. The vacuum chamber was pumped down into a high vacuum condition with a background pressure less than 2.0×10^{-3} Pa. In order to remove the top oxide layer the substrates were plasma cleaned in argon atmosphere ($2.0\ x10^{-1}$ Pa) for 30 minutes at negative pulse substrate bias voltage of 500 V and frequency of 250 kHz. A mixture of argon and nitrogen gases was introduced into the chamber during the process. The ratio of argon was kept a constant (25 sccm) and the nitrogen content was controlled by plasma optical emission monitor (OEM) with a feedback control. The information on the variation of the OEM signal (the plasma characteristics) with changes in the process parameters and the correlations between the signal and the deposition rate, morphology and structure of the coatings, are very important for optimization of the deposition process.

In the current experiments, a substrates temperature of 150°C for deposition of the coating was used. During the deposition substrates were biased with a pulse power source to induce proper ion bombardment on the growing surface to assist the formation of coatings with a dense structure. The experiments were conducted at bias voltage of -70 V and frequency of 150 kHz in DC work regime of the Ti and Cr cathodes and pulsed regime of the Al cathodes. The deposition started with sputtering of a Cr adhesion layer and after that a Cr-N interlayer with thickness of 200 nm was deposited reactively. Following these two layers, the fractions of Ti and Al increased to form a compositionally graded Cr-Ti-Al-N film, and finally Cr-Al-Ti-N with constant composition was obtained. The relative concentration of Cr, Ti and Al in the coatings was adjusted through the sputtering power, applied to the targets during deposition: P_{Cr} = 1.5 kW; P_{Ti} = 2.4 kW; P_{Al} = 0.6 kW.

Characterization techniques

The mechanical properties such as nanohardness and adhesion of the as-deposited and annealed CrTiAlN coatings 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 CCD camera, installed together on the same platform. Nanoindentation was performed by a triangular diamond Berkovich pyramid. The adhesion strength of the coating to the substrate was evaluated using MST equipped with a spherical Rockwell indenter with a radius of 200 μm under progressively increasing pressing force in a range of 1-30 N.

The studies of the coating morphology were carried out by Atomic force microscopy (AFM) using NanoScope VAFM (Bruker Inc.) equipment in air in tapping mode. Silicon cantilevers with reflective aluminium coating with thickness of 30 nm, Tap 300Al-G (Budget Sensors, Innovative solutions Ltd, Bulgaria) were used.

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

The chemical bonding of the coatings was studied by X-ray photoelectron spectrometry. XPS spectra were acquired on a Kratos AXIS Supra photoelectron spectrometer using a monochromatic Al Ka source with energy of 1486.6 eV. The binding energies were corrected relative to the C1s peak at 285.0 eV. The concentration of the elements was derived on the basis of the core level peak areas, corrected by the corresponding relative sensitivity factor values.

RESULTS AND DISCUSSION

The mechanical properties stability is of a main importance when the ceramic materials are used for industrial applications. Their structure contributes to this stability as it will be discussed in the following sections. In order to evaluate the thermal stability of the designed multicomponent CrTiAlN coatings, annealing tests were performed in circulating argon and atmosphere using a thermal furnace with a maximum temperature of 1100ºC.

The coated specimens were carefully degreased using suitable solvents and annealed at different temperatures (400ºC, 600ºC, 700ºC and 800ºC) for 2 h at each temperature, and after that were naturally cooled down to room temperature in the furnace. The alteration of the morphology, microstructure, chemical composition, hardness and adhesion strength after the treatment was analyzed.

Mechanical properties

Mechanical and tribological properties of the same as-deposited multicomponent coatings with a composition $Cr_{0.68}Ti_{0.19}Al_{0.13}N$ and a thickness of 2,1 µm were reported in our previous work [14]. So far no one has reported in the literature high-temperature mechanical properties for such coatings obtained at a low deposition temperature.

1. Hardness and Elastic modulus

Hardness and Elastic modulus of the as-deposited and annealed CrTiAlN/HSS coatings were characterized by dynamical nanoindentation in the loading interval of 10-100 mN and calculated from the load-penetration depth curve using the Oliver and Pharr method [15]. The maximum indentation depth was set at 200 mN which is less than 10% of the coating thickness, to avoid the influence of the substrate. An influence of the annealing temperature on the evolution of hardness and elastic modulus of the CrTiAlN coatings is presented in Fig.1.

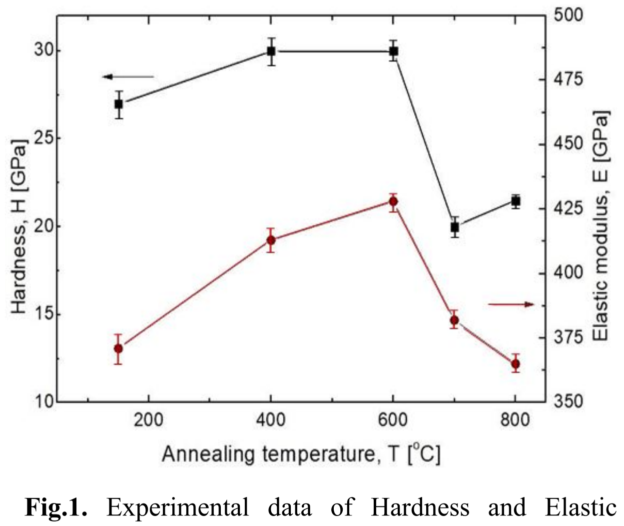


Fig.1. Experimental data of Hardness and Elastic modulus of the CrTiAlN/HSS coating as a function of annealing temperature

The nanohardness of HSS substrate in as-deposited state and after annealing at the 700°C was determined to be 11.0 GPa and 7.0 GPa, respectively. From the above experimental results it can be seen, that the hardness and elastic modulus show a similar behaviour. After annealing at 400°C and 600°C the hardness and elastic modulus increased from 27 to 31 GPa and from 396 to 426 GPa, respectively. However, as the annealing temperature increased to 700°C, significant change in the coating hardness and elastic modulus (Fig.1) was observed [16, 17]. This could be related to defect annihilation and stress relaxation. As a result the hardness and elastic modulus decrease. The change in mechanical properties is accompanied by a sharp change in morphology of the coating (see Fig.6) accompanied with grain enlargement and drastically increase of the surface roughness as compared to its smooth surface in as-deposited state. Reverse trend was observed for the effect of the annealing temperature of 800 °C on the hardness that was slight higher than for the samples treated at the temperature of 700°C.

2. Scratch resistance

A Rockwell diamond indenter (cone apex angle 120º, tip radius R=200 µm) was used to perform scratch tests. The applied load was linearly increased from 1 N up to 30 N with a constant scratch speed of 0.5 N/min. Series of scratch tests were performed before and after thermal treatment on coatings to obtain a load where the coating exhibits failure termed as the critical load (Lc). The critical load 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 (Ft) signals. Penetration of the indenter into the surface causes bending of the coating where both compressive and tensional stresses appear. The friction force between surface and sliding tip causes compressive stress in front of the moving tip and tensile stress behind it.

Excellent adhesion results without failures within loading range of 1-30 N were demonstrated by the as-deposited CrTiAlN/HSS coatings. A typical scratch graph and optical micrograph of the main scratch track part (Fn=25÷30N) of the coating and scratch test results of the acoustic emission (AE), friction force (Ft) and coefficient of friction (µ) are shown in Fig.2. As can be seen, no picks of AE and no changes of Ft were observed. The coefficient of friction of the coating against diamond indenter was measured to be µ= 0.09. No visible changes in the coating adhesion were observed after annealing up to 400°C. After annealing at 600°C, it was observed that with increase of the scratch length and the normal load respectively, the values of the friction force and coefficient of friction change. Very slight semi-circular tensile cracks were observed at the normal load > 20 N within the track. The friction force increased from 2.6 N to 3.4N, and the coefficient of friction from 0.09 to 0.12.

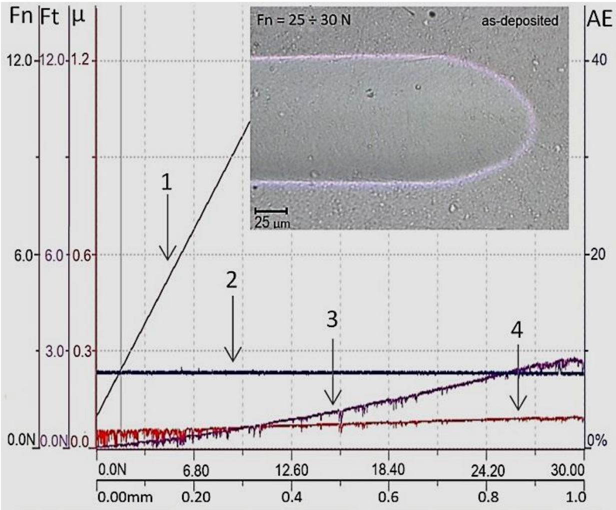


Fig.2. Scratch graph of the as-deposited CrTiAlN/HSS coating and optical micrograph of the main part of the scratch track: 1) Normal load; 2) Acoustic emission; 3) Friction force; 4) Coefficient of friction

After the annealing at a temperature of 700°C the coatings kept good adhesion properties. Only slight brittle tensile and micro-chevron cracks within and outside the track without chipping and spallation were observed (Fig.3). As a result, the friction force increased to 3.7 N and the coefficient of friction to 0.13. This change may be due to an increase of the stress between the substrate and the coating on as well as the formation of a thin, brittle oxide layer on the coating surface.

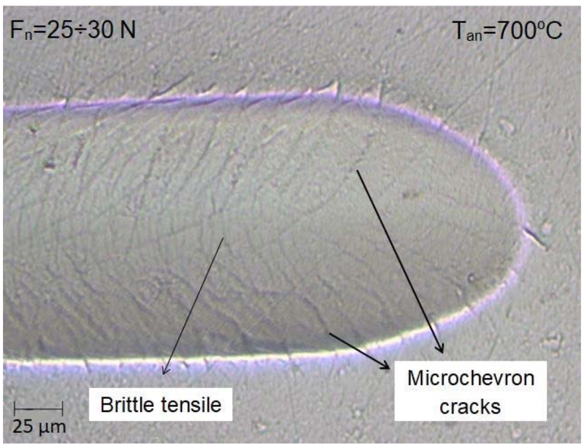


Fig.3. Optical micrograph of the main part of the scratch track obtained after annealing of the CrTiAlN coating at 700°C

After the next annealing of the coating at a temperature of 800°C no failures in the scratch track were observed. However, the brittle tensile and micro-chevron cracks are more pronounced. In this case, a noise in the acoustic emission signal was registered. As a result, an increase in the friction force up to 5.0 N and the coefficient of friction up to 0.18 was determined.

Coating morphology

1. AFM and SEM surface analyses

Effect of the thermal treatment on the CrTiAlN/SS coating morphology was studied by AFM. The AFM data (Fig.4) revealed that the as-deposited coating exhibited a low roughness and densely packed structure [14], consisting of well separated grains with apparently spherical form and predominantly equal sizes. Sporadic small defects were observed on the coating surface which leads to an increase of the roughness. The average roughness (Ra) and root mean square (Rq) roughness were obtained on a scanned area of 10 µm x 10 µm as follows: Ra = 20 nm and Rq = 26 nm.

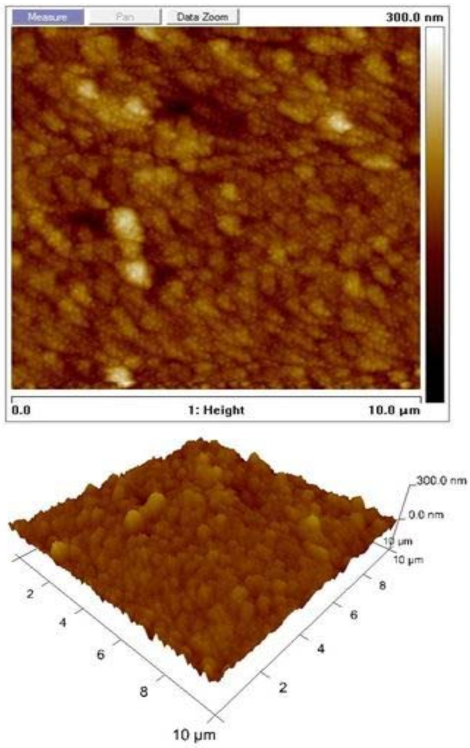


Fig.4. 2D and 3D AFM images of surface topography of the as-deposited CrTiAlN coating

SEM observation of the same as-deposited coatings revealed a similar feature (Fig.5). The coating surface showed columnar boundaries and the average columnar diameter was scattered between 150 to 300 nm. The coatings are dense and no cracks on the surface were disclosed which indicates a good compactness. No visible differences after the coatings treatment at 400°C and 600°C were observed.

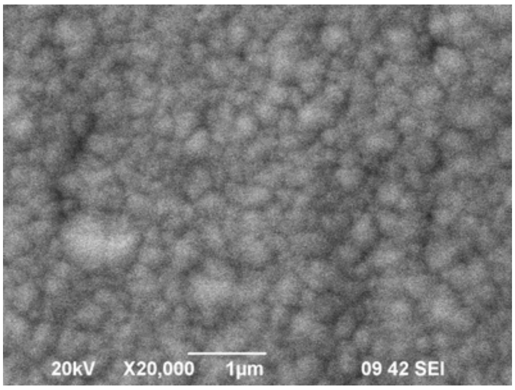


Fig.5. Surface SEM micrograph of the as-deposited CrTiAlN coatings

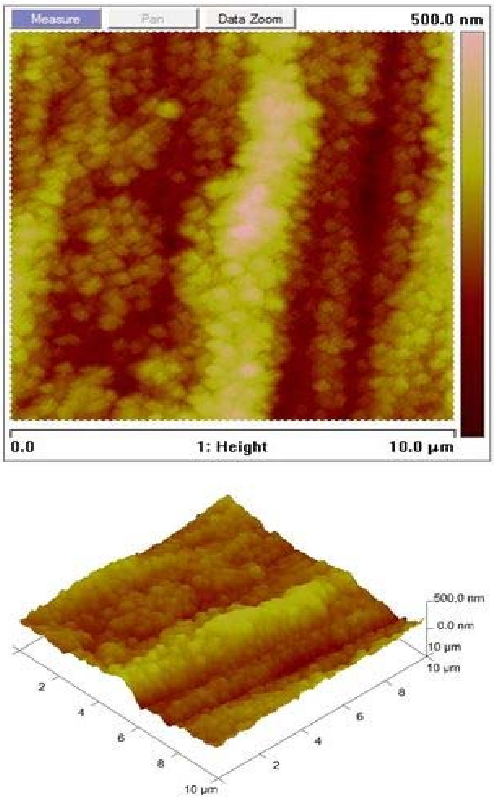


Fig.6. 2D and 3D AFM images of the surface topography of the CrTiAlN coating after annealing at 700°C

As Fig.6 (above) shows, after annealing at temperature of 700°C the average roughness and root mean square surface roughness obtained on the same area (10 µm x 10 µm) increase significantly. The calculated values of Ra and Rq in this case were 62 nm and 78 nm, respectively. According to the results shown in Fig.6, it could be concluded, that after the thermal treatment at 700°C the surface topography changes as a result of the stress, grain enlargement and the formation of the oxide phases on the coating's surface [18-20]. The increased surface roughness causes increase of the coefficient of friction as the scratch test showed.

Coating composition and chemical bonding

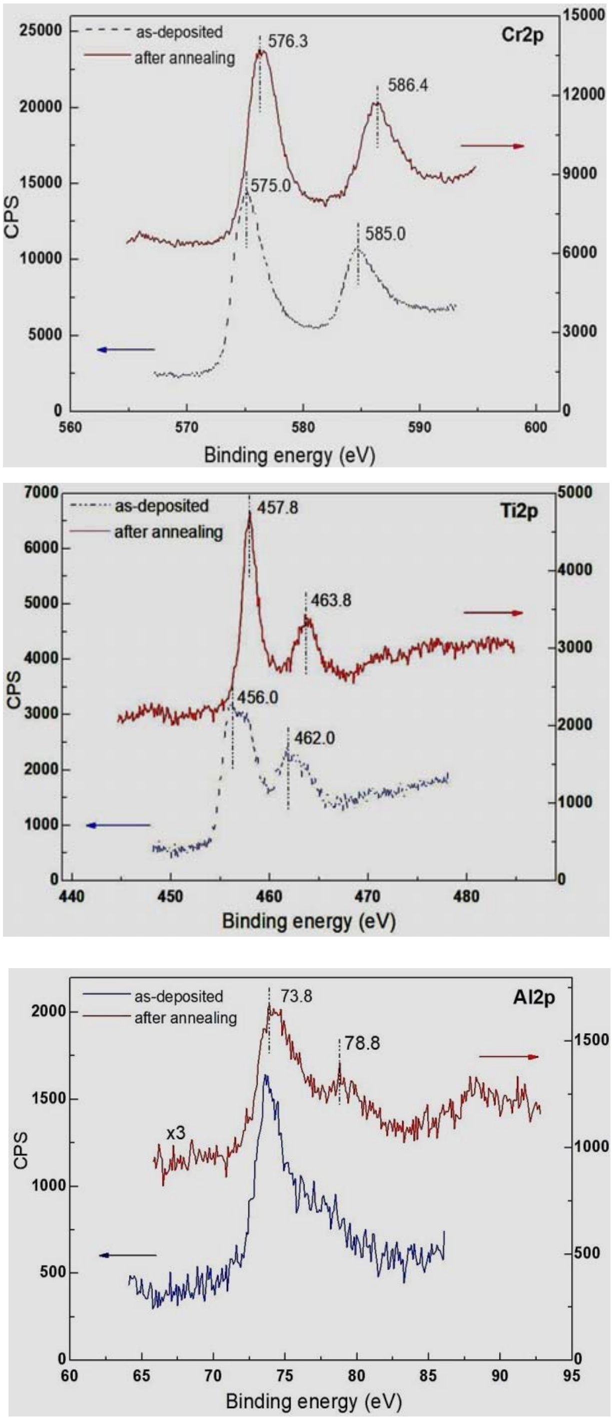
The EDS and XPS analyses were carried out to determine the existence of certain elements and amount of each element present. The evaluated elemental composition of the CrTiAlN coatings before and after annealing is presented in Tab.1.

Table1. Composition of the CrTiAlN coating

CrTiAlN coating	Elemental concentration (at. %)				
	Cr	Ti	Al	N	O
	as-deposited state				
EDS	30.95	9.06	6.24	53.75	
XPS	24.5	7.0	4.8	40.1	23.6
	after annealing at 700°C				
EDS	36.91	10.44	7.14	45.52	
XPS	19.1	5.5	2.7	10	62.7

The EDS and XPS analyses exhibited difference in elemental concentration of the coatings. It is seen that on the surface (XPS data) the concentration of nitrogen decreased four times, while the content of metallic elements is decreased by 20-25%. Besides, after annealing the concentration of oxygen increased three times. As the XPS analysis was performed without surface ion etching, the reduction of metal nitrides concentration is due to the formation of oxides on the coating surface after annealing. Based on the data from EDS and XPS analyses, the coating chemical composition after annealing was determined to be $Cr_{0.68}Ti_{0.19}Al_{0.13}N$ and $Cr_{0.7}Ti_{0.2}Al_{0.1}N$, respectively.

The chemical bonding status of CrTiAlN coatings was determined by XPS analysis. Typical XPS spectra of Cr2p, Ti2p, Al2p, N 1s and O1s energy regions for as-deposited and annealed CrTiAlN samples are shown in Fig.7. In the Cr2p spectrum the peaks centred at 575.1 eV and 585 eV could be attributed to Cr-N bonds for as-deposited coatings [10, 11]. The coating after annealing process shows similar Cr2p3/2 spectrum as that obtained in the as-deposited state. However, the main peak shifted to energy at 576.3 eV and the second one to 586.4 eV. These peaks could be attributed to formation of Cr-nitride and Cr_2O_3 oxides. The peak associated with Ti consists of two peaks centred at 456.0 eV and 462.0 eV. These peaks originate from Ti 2p3/2 and Ti 2p1/2 electrons in titanium nitride and oxynitride. After annealing the binding energies of Ti2p peaks are shifted to energies at 457.8 eV and 463.8 eV, corresponding to the TiNO and Ti_2O_3 bonds [18]. The Al2p spectra contribution with maximum binding energy of 73.7 eV is assigned to Al-N chemical bonding state within the coating.



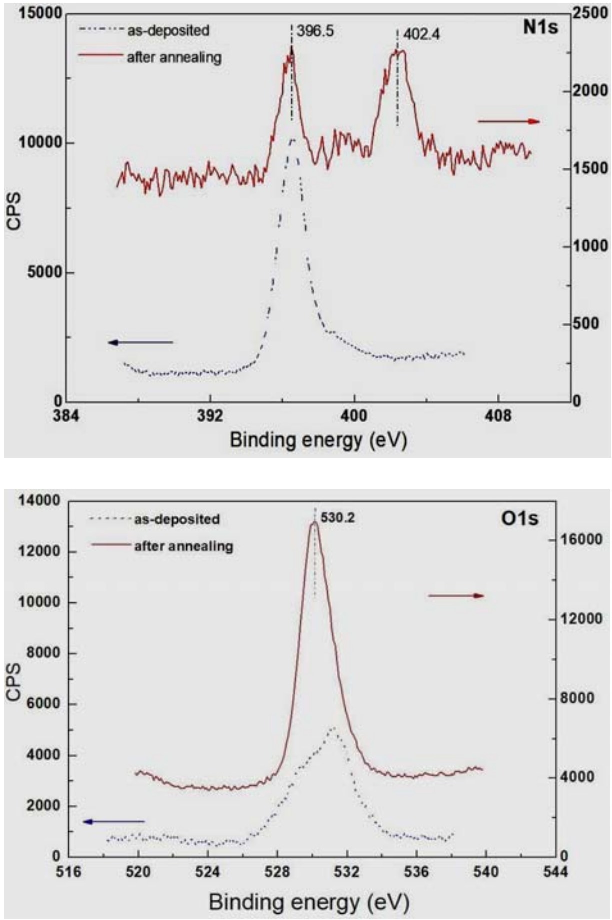


Fig.7. XPS spectra of Cr 2p, Ti 2p, Al 2p, N1s and O 1s on the as-deposited and annealed CrTiAlN coating

The annealing results in appearance of a small second peak with the binding energy at 78.8 eV which origin is not clear. Since the Al2p and Cr3s spectra overlap, the second peak could be attributed to Cr_2O_3 oxides.

The N1s spectrum of the as-deposited coating shows only one lightly asymmetrical peak with binding energy of approximately 396.5 eV which is attributed to the presence of metal nitrides (CrN, TiN and AlN) [19,20,21]. The chemical analysis showed presence of two peaks with low intensity situated at 396.5 eV and 402.4 eV after annealing. A possible explanation is the reduction of the metal nitrides concentration on the coating surface due to the formation of oxy-nitrides [22].

The O1s strong spectrum with a peak at 530.2 eV after annealing showed very high intensity in comparison with the same spectrum of the as-deposited coatings. It can be assigned to formation of oxy-nitride and oxides such as TiNO, CrO_3, Cr_2O_3, and Al_2O_3. The chromium oxide appearance after annealing has been well documented as being an exothermic reaction that normally takes place above 700 °C as reported in [2, 23, 24]. The above studies show that the mechanisms of Cr-Ti-Al-N thermal stability depend strongly on the elemental concentration. It can be stated that the oxidation process of the CrTiAlN coating is controlled mainly by the outward diffusion of Cr, Al, Ti and N species and by the inward diffusion of oxygen. As the coatings become more Cr-rich the preferential oxide formed might be mainly Cr_2O_3.

CONCLUSIONS

The CrTiAlN coating with a small amount of Al was successfully obtained using the closed-field unbalanced magnetron sputtering technique at the low deposition temperature of 150°C without additional substrate heating. The coating demonstrated good mechanical properties in the as-deposited state: nanohardness value of 27 GPa, an excellent adhesion in the loading interval from 1N to 30N and a low coefficient of friction (μ=0.1) in the as-deposited state.

After annealing at 400°C and 600°C the hardness and elastic modulus increased from 27 GPa to 31 GPa and from 396 GPa to 426 GPa, respectively and then decreased with further increase of the annealing temperature. With the increase of the tested temperature to 800°C, the coating demonstrated a hardness and elastic modulus of 22 GPa and 365 GPa, respectively. The friction coefficient of the coating tends to increase to the value μ= 0.18 as no failures in the coating were observed.

The AFM study revealed that the CrTiAlN coating exhibited a higher roughness after annealing. After the thermal treatment at 700°C the surface topography changes as a result of the stress, grains enlargement and the growth mainly of a chromium oxide phase on the coating's surface. The SEM and XPS studies revealed that the mechanisms of the Cr-Ti-Al-N thermal stability depend strongly on the elemental concentration. It was stated that the oxidation process of the coating is mainly controlled by the outward diffusion of Cr, Al, Ti and N species and by the inward diffusion of oxygen. The surface of the coating does not significantly oxidized after continuous heating up to 800°C, implying a better oxidation resistance.

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