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PROPERTIES OF TITANIUM NITRIDE COATINGS DEPOSITED BY A HYBRID CAE-PLD TECHNIQUE

WŁASNOŚCI POWŁOK AZOTKU TYTANU TiN NANOSZONYCH TECHNIKĄ CAE-PLD

The results of an investigation of the structure and properties of TiN coatings deposited by a hybrid CAE-PLD method are presented in the paper. The TiN coatings were synthesized on the HS6-5-2 tool steel substrates by a combination of pulsed laser ablation (PLD) and cathodic arc evaporation (CAE) methods. A KrF excimer laser, operating at wavelength of 248 nm, was applied for ablation of Ti target in a nitrogen atmosphere. All experiments were carried out at two values of the laser beam fluence (5 J/cm^2, 12 J/cm^2) and at constant: nitrogen pressure (0.5 Pa), substrate bias voltage (-250 V) and arc current (80 A). The CAE was used for a vapor excitation. The surface morphology, structure and chemical composition of the deposited coatings were analyzed by means of scanning electron microscopy, X-ray diffractometry, glow-discharge optical emission spectroscope, while mechanical properties of coatings (hardness, Young's modulus and adhesion strength) were determined using nano-indentation method and scratch testing. A comparative analysis of the properties of TiN coatings deposited by CAE method and by the hybrid CAE-PLD technique showed an increased hardness and an improved adhesion for CAE-PLD coatings. Moreover, it is observed that defectiveness degree of the TiN coatings deposited by CAE-PLD decreases with increasing of fluence value.

W pracy przedstawiono wyniki badań struktury i własności powłok azotku tytanu TiN nanoszonych techniką CAE-PLD. Powłoki TiN zostały naniesione na podłoże ze stali szybkotnącej HS6-5-2 w wyniku kombinacji dwóch metod: osadzania laserem impulsowym PLD (Pulsed Laser Deposition) oraz katodowego odparowania łukowego CAE (Cathodic Arc Evaporation). Do ablacji użyto lasera excimerowego KrF o długości fali 248 nm. Badania prowadzono zmieniając fluencję (5 J/cm^2, 12 J/cm^2) oraz przy stałym ciśnieniu azotu i stałych parametrach prądowych. Morfologię, mikrostrukturę oraz skład chemiczny osadzonych powłok zbadano za pomocą skaningowego mikroskopu elektronowego (SEM), dyfraktometru rentgenowskiego (XRD) oraz optycznego spektrometru emisyjnego z wyładowaniem jarzeniowym (GDOES). Do badania własności mechanicznych (twardość, moduł Younga, adhezja) użyto nanotwardościomierza oraz scratch testera CSM Instruments. Analiza własności powłok TiN nanoszonych techniką CAE oraz CAE-PLD wykazała większa twardość oraz adhezję powłok naniesionych techniką CAE-PLD w stosunku do tych samych powłok naniesionych metodą CAE.

1. Introduction

Pulsed Laser Deposition (PLD) is one of the simplest techniques among all PVD methods, which are versatile use to produce crystalline thin coatings. However, in spite of the simplicity of system set-up, the application of PLD technique to fabricate anti-wear, tribological coatings for industrial application have been yet mainly confined to the research environment. This is due to:

- the area of deposited material is too small for large substrates and the plasma plume crated by laser ablation have highly forward-directed spatial distribution thus coating's thickness is highly uniform [1,2],
- the adhesion of the anti-wear tribological coatings deposited on the steel substrates at low temperature by PLD technique is in many case very poor [3,4].

The first problem can be resolved by scanning the laser focused beam across the target surface, substrate rotating or moving during deposition, as well as by using multi-beam systems [5]. The second limitation can be overcome by using for realization coatings process combination two or more techniques such like that synergistic effect are obtained. Such a combination of the coatings techniques was called hybrid vapor deposition process. Although the possibility of various PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition) methods connection with PLD technique is unrestricted,

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only two hybrid methods were applicable by today for deposition of coatings:

- Radio Frequency – Pulsed Laser Deposition (RF-PLD) technique
- Magnetron-Sputter-Assisted Pulsed Laser Deposition (MSPLD) technique

In the hybrid RF-PLD technique r.f. plasma was used for substrate surface cleaning and heating, as well as for intensification of ion bombarding process of the growing coating, which is formed by atom flux created during laser ablation [6,7]. In the past, the pulsed laser deposition assisted by 13.56-MHz ratio frequency (r.f.) plasma was employed for deposition of: cubic boron nitride [7], titanium nitride [8], carbon nitride [9], amorphous carbon and Diamond Like Carbon (DLC) coatings [10-12].

MSPLD hybrid method generally was used for deposition of DLC coatings with multilayer architecture where super hard external layers are separate from relativity soft substrate by supporting interlayer. These interfacial layers, having good elastic modulus reduce stress, cracks propagation and improve adhesion of the DLC layer [13,14,15]. In MSPLD hybrid technique magnetron sputtering was applied for fabrication of interfacial layers while the PLD method has been applied for formation of DLC coatings. By using of the MSPLD hybrid technology the multilayer: TiC/DLC [13], WC/DLC [14] and graded Ti/TiC/DLC [16,17], Ti/TiN/Ti(C,N)/TiC/a-C [18] coatings were successfully deposited.

In practice, titanium nitride is widely used as a coating for tools and machinery parts what improves their mechanical and tribological properties [19]. The current paper describes hybrid deposition technique of TiN coatings. The applied CAE-PLD method uses cathodic arc evaporation (CAE) which are additionally accelerated and ionized by highly ionized plasma generated by pulsed laser ablation of titanium atoms from a target in a nitrogen atmosphere. The influence of deposition process parameters on the structure and properties of deposited TiN coatings was investigated.

2. Experimental

The TiN coatings were deposited on mirror polished (Ra=0.01 μm), 30 mm in diameter and 12 mm thick disks made of hardened HSS steel (63 HRC). In this method the coatings were synthesized by pulsed laser ablation of Ti target (purity 99,7%) in nitrogen atmosphere using KrF excimer laser operating at radiation wavelength of 248 nm and pulse length of 25 ns in combination with CAE (cathodic arc evaporation) method (Fig.1). The average distance between the arc sources and the substrate holder was 400 mm and the distance from surface of the substrate to the ablated target was 40 mm. Prior to deposition process, the substrates were ultrasonically cleaned in trichloroethylene baths. All deposition experiments were performed in high vacuum chamber, which was evacuated to base pressure of 2,5x 10^{-3} Pa. Before coating process the substrates were also ion-cleaned and preheated to temperature of approximately 300° C, using titanium arc source, operating at arc current of 80 A. The substrates were biased to -1000 V potential during these operations. Deposition of the TiN coatings by hybrid method was conducted under the following condition: nitrogen pressure (0.5 Pa), negative bias voltage (-250 V), arc current (80 A), laser fluence (5 J/cm^2 or 12 J/cm^2) and deposition time (50 min). The total coatings thickness measurements were carried out by ball- cratering method (Calotest CSEM). The surface roughness of samples before and after coating deposition was determined using a Hommel Tester T 2000 profilometer. The structure of TiN coatings was identified by means of X-ray diffraction technique (XRD) and their surface morphology was observed using scanning electron microscopy (SEM). The investigation of the size and distribution of the coating defects was performed by the optical microscopy equipped with digital image analyzer. Quantitative chemical analysis of the coatings as a function of coating depth was determined using glow-discharge optical emission spectroscopy (GD-OES). Coating hardness and Young's modulus were determined from the loading and unloading curves, carried out with an ultra low load depth sensing Nano-Hardness Tester NHT CSEM equipped with a Berkovich diamond indenter. An indentation depth of 90 nm was used for every measurement. Substrate-coating adhesion was measured using conventional scratch testing (CSEM Revetest). During each adhesion test the normal load was increased from zero up to 100 N.

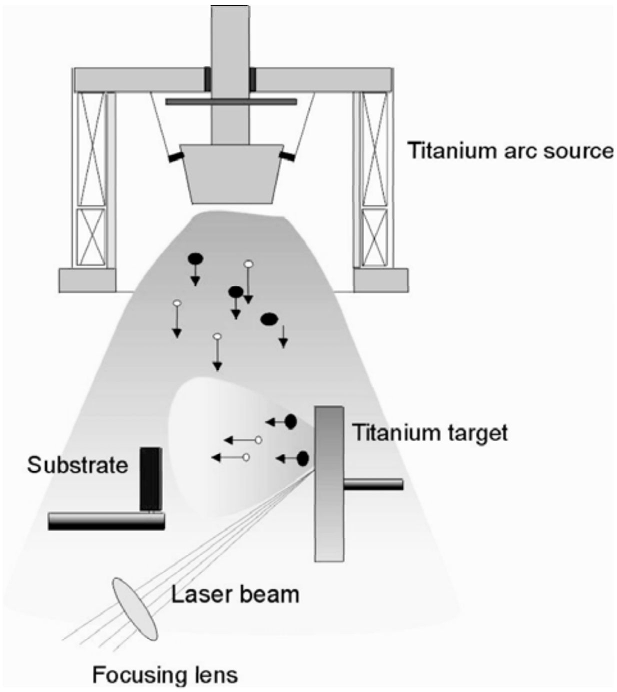

Fig. 1. Schematic drawing of equipment configuration for the hybrid CAE-PLD technique

3. Results and discussion

Thickness and surface morphology of the coatings

Results of measurements of coating thickness and deposition rate are summarized in Tab. 1. TiN coatings deposited by hybrid CAE-PLD method on the HSS substrates have the similar thickness 1200-1300 nm and are thicker than the coatings (900 nm) which were deposited by using arc evaporation. These results clearly showed that the deposition rate for CAE-PLD technique is above 30% higher in comparison with the deposition rate of CAE method. It was also found that an increase of laser fluence from 5 J/cm^2 to 12 J/cm^2 does not influence the deposition rate.

TABLE 1
The values of coating thickness and deposition rate measured for CAE and CAE-PLD techniques

Coating	Thickness of the coating (nm)	Deposition rate (nm/min)
TiN CAE-PLD 1	1300	25
TiN CAE-PLD 2	1200	24
TiN CAE	900	18

Such a course of change of the deposition rate with increasing of fluence for hybrid CAE-PLD method could be due to a partial re-sputtering which occurs during the deposition process when highly energetic ions attack the surface of the deposited coating. It is well known that the efficiency of re-sputtering process, which always accompanies the coating growth during its deposition by PLD technique, directly depends on the energy of ions bombarding the coating surface [20]. For hybrid CAE-PLD method, when the fluence of laser beam increases, the highly ionized and energetic stream of Ti atoms is ejected from the titanium target. Such, highly ionized and energetic ions, makes the coating growth process more effective, however in the same time a large number of atoms is re-sputtered from the growing coating. The competition between these two opposite processes is manifested by little reducing the deposition rate.

The investigation of TiN coatings morphology produced by CAE-PLD method and by CAE showed that all coatings contain identical type of structural defects like microdroplets, pits and shallow craters (Fig.2). The diameter of these defects is in the range of 1,0-5,0 μm (Fig. 3). The defect densities (expressed by average number of defects per unit area) are shown in Fig.4 and the surface roughness of the investigated TiN coatings are reported in Table 2. Presented results the coatings quality clearly indicate that the TiN coatings deposited by hybrid CAE-PLD technique are smoother than such coatings manufactured with the use of CAE. Moreover, the surface defects density of the CAE-PLD deposited coatings decreases with increasing of laser fluence from 5 J/cm^2 to 12 J/cm^2. Such a trend of defectiveness ratio changes with the increased laser fluence could be explained as caused by the collisions of high energetic ions created during laser ablation with droplets generated by CAE and PLD process. Interaction of these ions moving towards the substrate with smaller microdroplets may cause their evaporation before they achieve the surface of the substrate [21]. Furthermore, evaporation of the droplets in CEA-PLD process is supported additionally by high temperature (about 20000 K) of the plasma plume, warmed up by absorption laser radiation as an effect of inverse-Bremsstrahlung phenomenon [22]. All of this indicated above mechanisms of microdroplets evaporation may explain decreased number of defects on the CAE-PLD coating surfaces (Fig4).

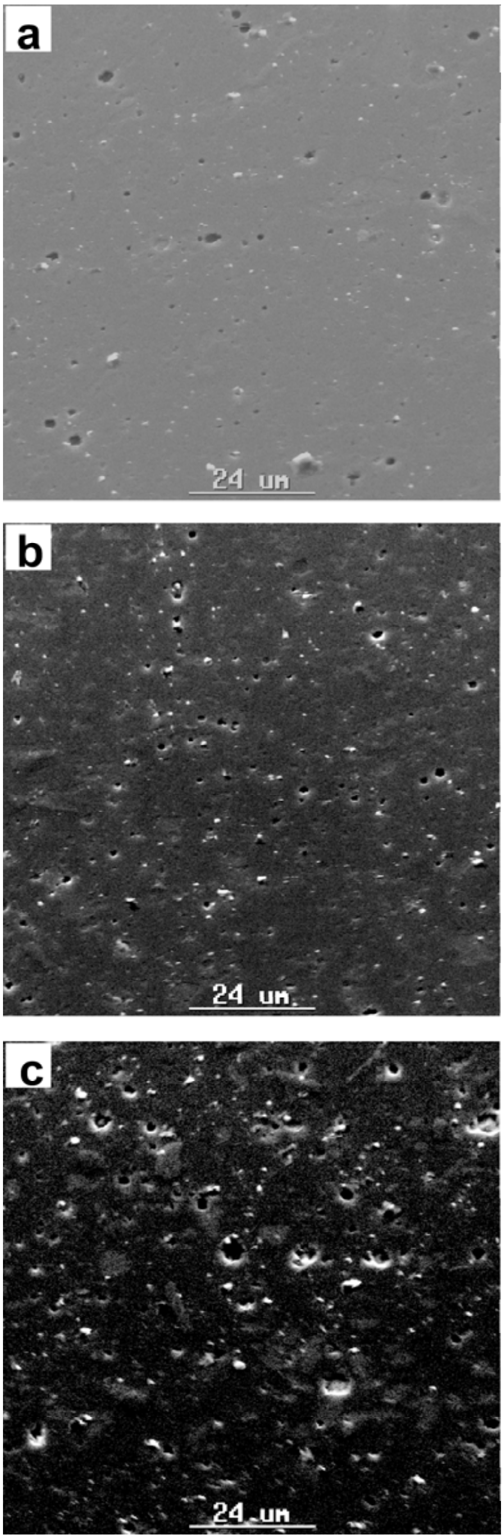

Fig. 2. SEM image of the surface of TiN coatings on HSS substrates deposited by: (a) CAE-PLD method using a fluence of 5 J/cm^2 (b) CAE-PLD method using a fluence of 12 J/cm^2 (c) CAE method

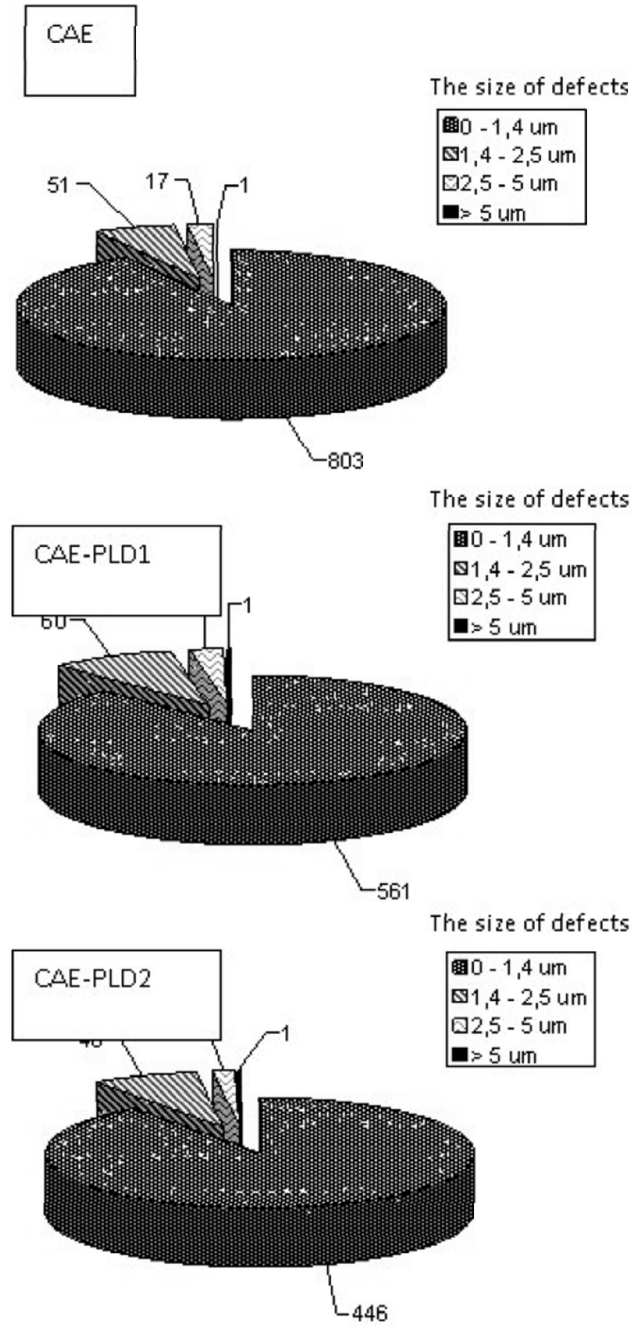

Fig. 3. The result of droplet size and quantity measurements (CAE, CAE-PLD1, CAE-PLD2)

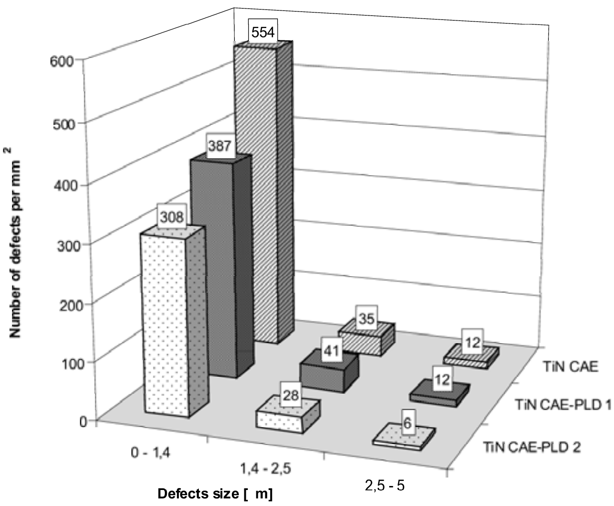

Fig. 4. The average number of defects per unit area for TiN coatings deposited by CAE-PLD and CAE methods

TABLE 2

Defects density and roughness of the TiN coatings deposited by CAE-PLD and CAE techniques

Coating	Roughness R_a (nm)
TiN CAE-PLD 1	100
TiN CAE-PLD 2	70
TiN CAE	270

Structural characterization and chemical composition of the coatings

XRD analysis showed that coatings deposited by hybrid CAE-PLD ,as well as, by the CAE method are composed of two phases: TiN and Ti (fig. 5). The coatings deposited by CAE-PLD method with using of lower fluence value show strong (111) preferred orientation. The weak peaks of (200) and (220) TiN phase are also visible on the XRD pattern. In case of TiN CAE-PLD 2 coating, the rise of the laser fluence leads to decrease of (111) and to increase of (200) TiN peak intensity. Such variation of preferred TiN coating growth, from (111) and (200), could be probably caused by relaxation of the residual stress in the coating. As the fluence increase the highly ionized flux of Ti atoms with higher kinetic energy emitted from the target impinge the surface of the coating. According to Davis [23] stress relaxation with increasing energy of the bombarded metal ions is determined by the process of defects annihilation (point and linear defects are generated during plasma assisted growth can be annihilated due to cascade ion collisions at the growing coating surface). On the basis of XRD analysis it was revealed that the content of Ti phase in the coating produced by hybrid CAE-PLD is two-tree time smaller than in the TiN coating produced by a CAE method. For all examined TiN CAE-PLD and TiN CAE coatings the average crystallite size estimated by Scherrer equation was between 17 and 18 nm. The results of GD-OES quantitative analysis of TiN coatings are given in Fig. 6. These results indicate that the CAE-PLD coatings deposited with using both fluence values were probably over-stoichiometric but their chemical composition is very similar to the TiN CAE coating. Although GDOES analysis did not permit confirmation of this over-stoichiometric, because calibration of GDOES method is difficult, it was evident from these studies that the energy of ions bombarding growing coating practically does not influence their chemical composition.

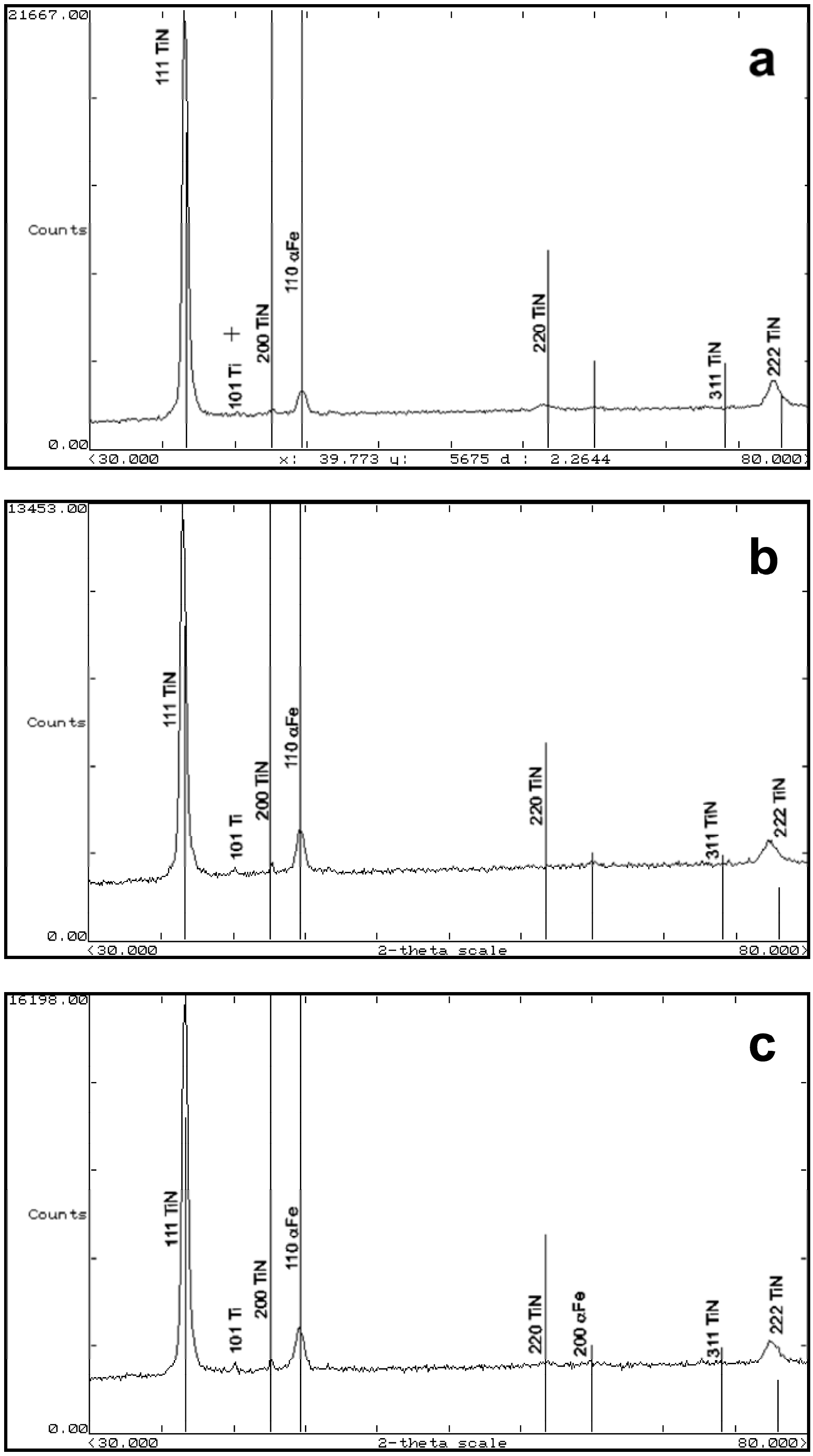

Fig. 5. XRD patterns of TiN coatings deposited by: (a) CAE-PLD hybrid method at a fluence of 5,0 J/cm^2 (b) CAE-PLD hybrid method at a fluence 12 J/cm^2 (c) CAE method

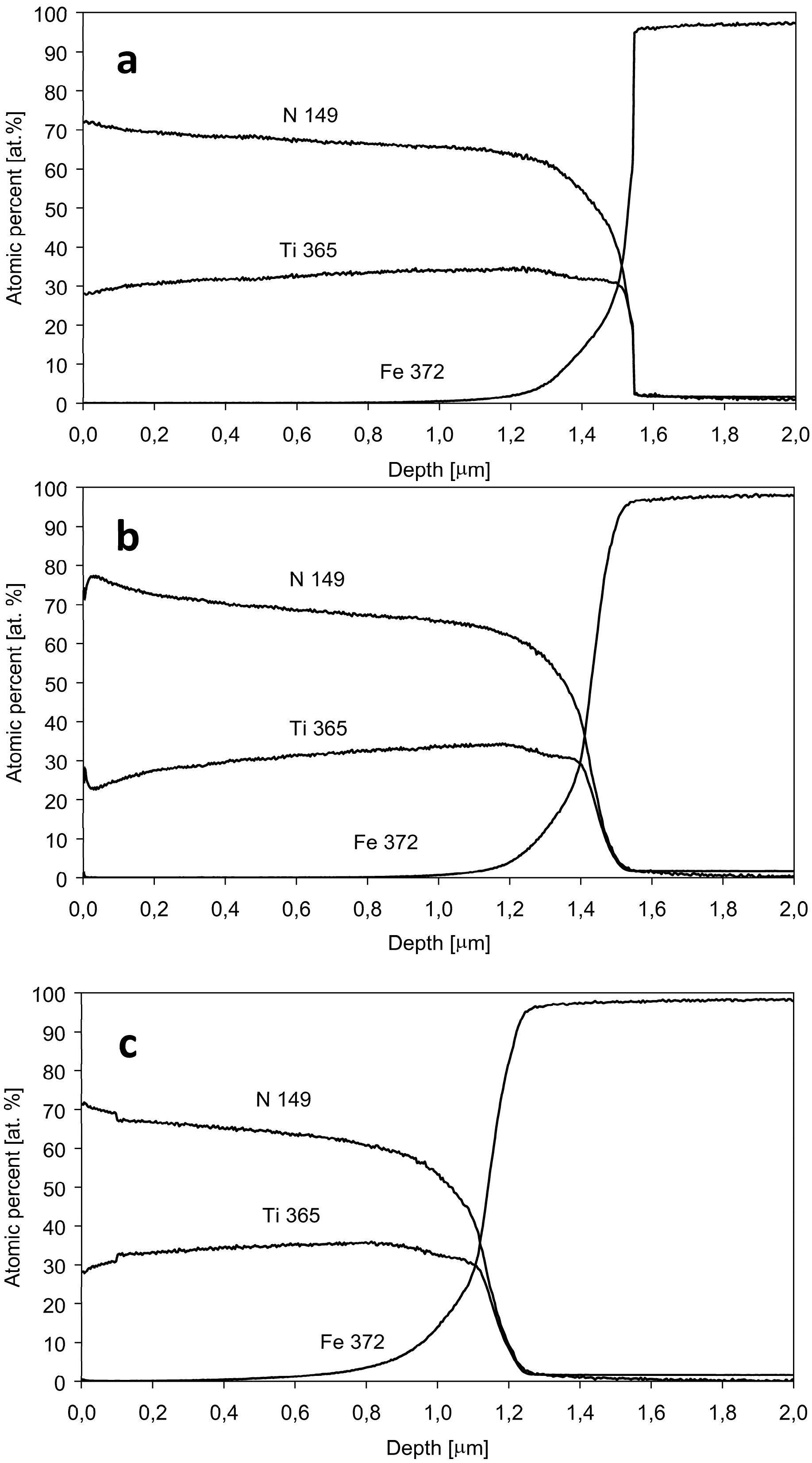

Fig. 6. GD-OES quantitative depth profiles of TiN coatings deposited by: (a) CAE-PLD hybrid method at a fluence of 5,0 J/cm^2 (b) CAE-PLD hybrid method at a fluence of 12 J/cm^2 (c) CAE method

Mechanical properties of the TiN coatings: hardness, Young's modulus and adhesion

Table 3 presents the results of mechanical properties (Young modulus, nanohardness and adhesion strength) investigations. The executed measurements proved that hardness and Young modulus of the TiN CAE-PLD coatings are slightly higher then those of the TiN CAE coatings. Nevertheless, the TiN coatings deposited by hybrid CAE-PLD technique showed better adhesion strength in the comparison to the coating deposited CAE method.

TABLE 3

Mechanical properties of TiN coatings

Coating	Hardness H (GPa)	Young modulus E (GPa)	Adhesion strength L_c(N)
TiN CAE-PLD 1	20	317	70
TiN CAE-PLD 2	19	322	71
TiN CAE	18	308	67

4. Conclusions

The results obtained in this work lead to the following statements:

1. The defectiveness of the TiN coatings deposited by CAE-PLD decreases with increasing of fluence value,
2. XRD analysis showed that all investigated coatings are composed of two phases: TiN and Ti,
3. Comparative analysis of the properties of TiN coatings deposited by CAE-PLD and by the CAE techniques showed an increased hardness, Young modulus and improved adhesion for CAE-PLD coatings. Also the smoothness of the coatings deposited by hybrid CAE-PLD technique is better than those of coatings deposited by CAE,
4. It has been shown that hybrid CAE-PLD technique is more effective for the deposition of TiN coatings than CAE technique.

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