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A Review on Titanium Nitride and Titanium Carbide Single and Multilayer Coatings Deposited by Plasma Assisted Chemical Vapor Deposition

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PAPER INFO	ABSTRACT
	In this paper, we reviewed researches about the titanium nitride (TiN) and titanium carbide (TiC) single and multilayer coatings. These coatings were deposited by the plasma assisted chemical vapor deposition (PACVD) technique. Plasma-based technologies are used for the processing of thin films and coatings for different applications such as automobile and aerospace parts, computer disc drives, food industry and surgical/medical instruments. We describe the state of the performance of different coating systems and thin film architectures in PACVD suitable for industrial-scale or laboratory applications. Mechanical properties of coatings such as wear resistance, hardness and the scratch resistance, structural characteristics, physical and chemical properties like coatings adhesion into different substrates, wetting behavior and corrosion resistance were studied. Thus, this paper represents a source of information for those who want to familiarize with the status of knowledge in the area of materials science of functional coatings, in particular TiN/TiC coatings that was deposited by a new Plasma-based technologies. *doi*: 10.5829/idosi.ije.2016.29.05b.12

1. INTRODUCTION

TiN and TiC have been identified as good materials for different applications, based on their thermodynamic stability and thermal shock resistance [1]. In addition, TiN coatings have good properties such as high fracture toughness and maintaining their stability at high temperatures. TiC coatings also have unique characteristics like high hardness and high elastic modulus and low coefficient of friction [2]. Application of these hard coatings are vast and include cutting tools, extrusion moldings [2], automobile and aerospace parts, machine parts [3], computer disc drives, precision instruments, surgical/medical instruments and human replacement organs [4].

Although TiC coating has beneficial properties, applications as a single layer coating has been limited

and that was related to the brittleness of the TiC phase which has a strong covalent bond. This limitation can be usually overcome by increasing the number of layers in coatings. In wear-resistant layers on cutting tools, since single-layer and hard coatings show less efficient and also less performance (due to specific characteristics) in compare to multilayer coatings [2, 5, 6]. In addition, one of the aims of multilayer deposition is to produce a fine-grained layer structure, in comparison with mono-layers, which mostly reveal a coarse-grained columnar structure, granular grown films have a better mechanical strength. The structure in multilayer coatings can be different from that of single ones as the oriented growth is changed by the composition and the structure of single layers [5].

To produce these coatings, physical and chemical vapor depositions (PVD and CVD) offer a large variety of material coatings, high experimental flexibility as well as minimization of waste disposal [7]. Advantages of the PVD are deposited materials with improved

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properties, deposited organic material and environmentally friendly process. Advantages of the CVD are high purity (typically 99.99-99.999%), high density (nearly 100% of theoretical), deposited material well below the melting point and economical in production. But in all, application of PVD methods, due to the low temperature, the low production rate and coatings adhesion may decrease. In CVD methods, Grain growth occurs and the quality of coating properties reduces due to the high temperature [8, 9]. In addition, to produce TiN or TiC by CVD, a thermally activated process, high deposition temperatures, above 1000°C, are needed. This is not a recommended method for steel substrates as overheating may occur above 600°C. The deposition temperature can be reduced below 600°C through activation of reactive gases with extra energy sources such as plasma [10]. Thus, the plasma assisted chemical vapor deposition (PACVD) is suitable for creating thin multilayer and single coatings on substrates, due to the possibility of achieving properties at low temperatures, high deposition rate, high throwing power and high adhesive strength [2, 11]. In addition, when PACVD use the pulsed direct current, it has great advantages. In this way the plasma can penetrate holes and narrow cracks in complex components [12, 13].

Many factors in coatings process like voltages, duty cycle, pressure, temperature and gas fluxes can have effect on coating properties [8]. Therefore, in depositing single or multilayer coatings by PACVD process, many researchers studied these parameters. In this paper we reviewed the papers about single and multilayer coatings of TiC, Ti(C,N) and TiN deposited by PACVD from 1991 to 2014 (nearly 25 years). The structure, and mechanical, chemical and physical properties of coatings were investigated.

a) Single Coating: TiC   In 1991, C. Taischner et al. [14] for the first time deposited TiC coatings on hard metal substrates (WC/Co) using a d.c. PACVD at 667°C. The TiC coatings were deposited from the gas phase with $TiCl_4$, hydrogen, argon and a carbon source (benzene or n-heptane). They reported that the film deposition rate was in the range $10-30/\mu m\ h^{-1}$ and coatings were smooth and had small grain size (10-30 nm). The measured Vickers micro-hardness passed through a maximum, dependent on the gas phase composition. No change in the structure and texture was observed by variation of the carbon source.

The existence of a diamond-like carbon component or states of excess carbon atoms in the TiC coating was studied by Oguri et al. [15] using laser Raman spectroscopy for obtaining a low friction coefficient.

Rie et al. [16] used metallo-organic precursors to deposit Ti(C,N) or Zr(C,N) layers. The effect of experimental parameters such as pressure and coating temperature and the precursor evaporation temperature

were studied. Their result showed that by decreasing coating temperature to 300°C was possible to deposit layers with no chlorine content on hard metals.

TiC/C, (Ti,Al)C and (Ti,Al)N layers by PACVD under D.C.-pulse discharge conditions discussed by Bartsch et al. [17]. They studied the composition and structure of coatings. Results showed that the friction coefficient of TiC layers decreased to 0.3. They also showed that oxygen impurities could cause a decrease in hardness of (Ti,Al)N layers. The layer stress decreased by about 50% as the thickness of single layers in multilayer coatings was about 100-300 nm.

TiC coatings were deposited by Jarms et al. [18]. The variable parameters in this paper were the partial pressure ratio of methane to titanium tetrachloride (P_{CH4}/P_{TiCl4}), the plasma voltage and the pulse/pause ratio. The result showed that small partial pressure ratios up to 15 resulted in nearly stoichiometric TiC coatings at high plasma voltage. Higher partial pressure ratios caused excess carbon, which bound as C-C or C-H. Increasing carbon content was found also for both increasing plasma voltage and increasing pulse/pause ratio. The layer hardness was found to decrease with increasing excess carbon. No significant influence of composition on the friction coefficient detected in this paper.

TiN, TiC and TiB2 were deposited by Pfohl et al. [19]. Composition, structure, hardness, adhesion, wetting behavior and corrosion resistance to aluminum melt were the variable parameters. The result showed that a proper PACVD coating could increase the lifetime by a factor of 130-300 with respect to an uncoated component.

TiCx and amorphous carbon were deposited from gas mixtures by Leonhardt et al. [20]. The effect of the gas ratio and hydrogen content on the layer composition and properties were investigated in this paper. The transmission electron microscopy (TEM) studies showed that the TiCx crystallites have a homogeneous distribution and a grain size of 4-7 nm. They had no preferred texture. The excess carbon and dissolved hydrogen could change the micro-hardness and surface roughness. The absence of dissolved hydrogen increased the micro-hardness to 4000 HV [0.02]. Thus, a good candidate for sliding wear applications may be a layer of TiC/a-C due to the low surface roughness. Kaestner et al. [21] studied the plasma diffusion treatment before depositing coatings. Their results showed that plasma nitriding and carburizing changed TiC coatings adhesion due to the plasma diffusion pretreatment and coating conditions. Plasma-nitrocarburizing pretreatment made better adhesion for the TiC coating. They claimed that the tribological applicability of TiAl6V4 was improved by the combination of plasma diffusion treatment and TiC coating. A duplex plasma treatment with shot-peening could improve the fretting fatigue and wear resistance.

Amorphous carbon (a-C) and TiC coatings were prepared by Liepack et al. [22]. It was shown that the carbon phase created a matrix with nanocrystalline TiC particles. TEM investigations revealed the occurrence of cracks in regular distances of approximately 400 nanometer (nm). They used the x-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) to study compositional details. The hydrogen content in the carbon phase was about 8–10 at.% [22]. The stress state of TiC, amorphous carbon (a-C) and TiC/a-C layers was determined by the measurement of the substrate curvature accordance to the layer thickness High compressive stress was found for the TiC layers independent of the layer thickness, whereas a-C layers yielded only a low compressive stress. The stress difference of two components was the reason for crack formation in composite layers leading to a stress relaxation increasing with the layer thickness [23].

The structure and corrosion sate of TiC coatings on hot-work steels (H11) was investigated by Shanaghi [24]. Grazing incidence x-ray diffraction (GIXRD) revealed that the (200) plane was the most stable plane in TiC coatings under thermodynamically stable conditions. They claimed that the TiC coating with a 40% duty cycle, showed high corrosion resistance in 0.5 M H_2SO_4 and 0.05 M NaCl media. Their results revealed that electrochemical properties and the duty cycles could affect the structure and morphology of coatings. As in PACVD technique, temperature and gas flux were two important variants which affect the coatings structure and mechanical properties; Azadi et al. [8, 25] analyzed mechanical properties of different TiC single coatings with these variable parameters. The deposition temperature changed from 490°C to 450°C and the flow rate ratio of methane to titanium chloride increased from 1.5 to 6. Results showed that TiC coating color changed due to the different CH_4 to $TiCl_4$ flow rate ratio. When the coating deposited at 450°C, the best mechanical properties such as high hardness (27GPa [25] or 3100 VHN [8] or 23GPa [26]), wear resistance, fracture toughness (11.3MPa. $m^{0.5}$) [8] and low surface roughness (18 nm) [8] were achieved.

b) Single Coatings: TiN   For the first time, in 1990 a new type of plasma reactor for the PACVD of TiN had been designed and built by Laimer et al. [27]. The reactor used an R.F. discharge operating at a pressure around 1 mbar and at a frequency of 13.56 MHz. Experiments showed that the uniformity of deposition on three-dimensional substrates depended on the substrate bias. At relatively high bias voltages, the layer on the edges had a different composition to that on plane surfaces, whereas at lower bias voltages uniform composition could be achieved. They demonstrated that TiN coatings of excellent quality can be deposited on all

surfaces of objects of complex geometry at low temperatures (450-550°C).

Radio frequency of PACVD without and with D.C. substrate bias, d.c. PACVD, pulsed D.C. PACVD and microwave plasma excitation were used by Freller et al. [28] to deposit TiN coatings. The microwave process created hard and adhesive coatings on high speed tool steel substrates. The d.c. pulse process had the best throwing power for narrow holes. They reported that all methods of the d.c. pulsed PACVD process were suitable for depositing TiN coatings on three-dimensional tools.

The use of a metal-organic precursor in PACVD process was applied in the paper of H.R. Stockt et al. [29]. Two volatile liquids ($Ti(N(CH_3)_2)_4$ and $Ti(N(C_2H_5)_2)_4$) were used along with hydrogen and argon. The total pressure applied in this method was 1 mbar. The steel substrates temperature during deposition was changed from 200°C to 500°C. The hardness of fine-grained polycrystalline layers measured more than 2000 HV, as they deposited up to a temperature of 400°C. By increasing the temperature to 500°C, the quality of the coating dominantly decreased.

Attempts had been made to identify the influence of the flow rate ratio of N_2-to-$TiCl_4$ (8-9) on TiN coatings characteristics by Oguri et al. [30]. Coatings were deposited on M2 steel and pure iron at the temperature of 550°C. When the N_2-to-$TiCl_4$ flow rate ratio changed, the composition and hardness of coatings remained constant, but the orientation of planes varied from (111) to (200) and from columnar to non-oriented.

In the paper of Rie et al. [31] metallo-organic compounds, titanium tetra kisdialkylamides, were used to deposit layers. It was shown that Ti (C,N) coatings with no chlorine content could be obtained by MOCVD even at temperatures lower than 450°C. Then, the structure of TiN layers deposited by PACVD onto steel substrates was investigated [32]. The nitrogen in this technique was in a molecular state (N_2^* and N_2^{+*}). Titanium was also found in the ionized state. The controlling factor for the layer growth was attributed to the Ti^+ intensity.

TiN films were created on M2 steel by Endle et al. [33]. At 500°C, TiN coating was formed with a (200) surface orientation and had a columnar zone 2 grain structure. At 400°C, an additional amorphous component with a zone T structure was found. Both types of films had good adherence with scratch adhesion critical loads comparable with values for the sputtered TiN. In the zone 2, films failed by cracking and occasional chipping within the coating. In the zone T, films failed by cracking in the coating and by chipping within the coating and by the interface. Auger electron spectroscopy (AES) depth profiling indicated that the interface was sharp and no accumulation of chlorine was observed. AES and scanning electron

microscopy (SEM) suggested that distinct TiN islands or nuclei were present in the early stages of growth.

Effects of surface properties on coating adhesion and wear behavior of PACVD-coated cermets in interrupted cutting was done by Tönshoff et al. [34]. They showed that by modifying the surface integrity of the substrates the life time of cermets could be increased by a factor of 1.5 in milling.

The dependence of bias voltages, pressure and gas flows on plasma properties and the deposition process was studied by Mogensen et al. [35]. Changing process parameters could cause large variations in the emitted light. The deposition rate depended linearly on the N^{+2} signal as the pressure and the N_2 flow changed. There was no measurable correlation between the OES signal and the deposition conditions.

Thomsen et al. [36] studied the residual stress in TiN layers. Process pressures, bias voltages, temperatures and partial gas flows were varied in an effort to obtain optimal coating properties. Total macroscopic stress values were found to range from -1.5 to 1.5 GPa. The lowest surface energy was related to plane of (200). When the residual stress was the lowest, a preferred orientation of texture was observed.

TiN coatings were deposited on high-speed steel (HSS) by Kim et al. [37]. Prior to the deposition, substrates were exposed to the NH_3 plasma in the PACVD deposition chamber. Then CrN was deposited on the substrates after the NH3 treatment. Results showed that lattice parameters of substrates increased after pre-treatment.

Coatings were adhesive when treated with NH3 compared with that without pre-treatment due to the removal of oxide from the substrate surface. As a result, the wear resistance was also improved due to the higher hardness and higher adhesion effect. The surface and cross section images of different coatings can be observed in Figure 1.

It was known that the residual chlorine was a significant drawback for PACVD coatings when chloride was used as precursor. The effort of Zhu et al. [39] had been focused on the preparation of the TiN coating with less chloride content. Argon-ion bombardment was employed at the beginning of the coating process when the coated layer was less than 100 nm thick. The high-energy argon ions were also helpful to densify the layer and decrease the residual chlorine content. Results showed that the bonding strength in this process was higher than that of the regular process. The corrosion resistance and wear resistance was even better than stainless steel.

TiN layers were deposited in different-sized PACVD reactors by Hardt et al. [40]. They studied the influence of different N_2–H_2 gas flow and the pause time on layer properties in relation to the reactor volume. SEM measurements showed that the growth rate increased with increasing N_2/H_2 gas flow ratio,
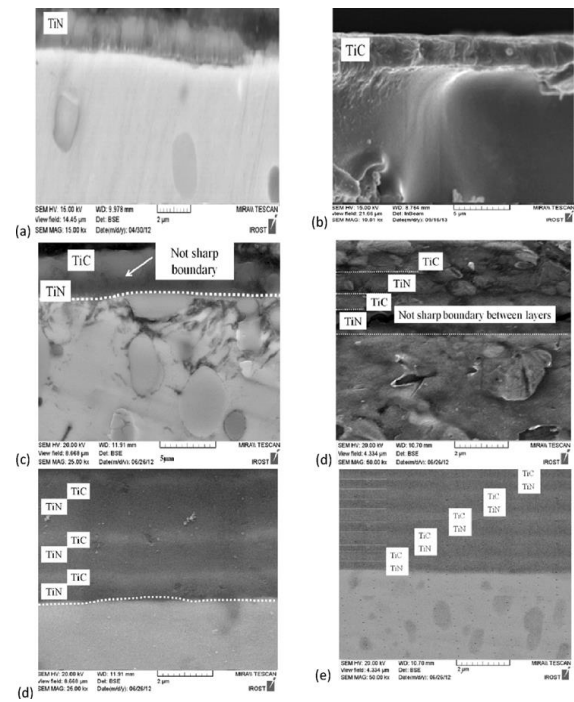
Figure 1. Cross section of SEM images for samples including (a) TiN; (b) TiC; (c) multilayer coatings of two layers; (d) multilayer coatings of four layers; (e) multilayer coatings of six layers and (f) multilayer coatings of ten layers [38]

whereas an influence from the total gas flow could not be found.

The TiN layers were nearly stoichiometric, except for low N_2 gas flows. GIXRD measurements revealed a transition from X-ray amorphous to crystalline TiN with higher N_2/H_2 gas flow ratios. However, a preferred orientation was not observed.

Parameters of TiN-PACVD process was discharge conditions like reactor size, current density (0.072–0.98 mA/cm^2) and N_2/H_2 gas inlet ratio (0.03–1.07) in the paper of Eckel et al. [41]. Results showed that a Ti$^+$ line emission was observed in the cathode glow, emissions of the other species were also detected in the negative glow. The spatial intensity distribution of the emission of various species was different. The growth rate and the film morphology mainly depended on the current density. The layer composition (Ti/N~1) only changed by essential small N_2 admixtures.

Gas mixtures of TiCl$_4$, AlCl$_3$, N_2, or methane/hydrogen/argon were applied to deposit hard crystalline (Ti,Al)N, TiC and TiN coatings on steel and WC-Co hard metal substrates at temperatures between 500°C and 700°C by uni-polar and bi-polar pulsed D.C. PACVD techniques by Taschner et al. [42]. The golden, violet grey or dark grey colored TiN, (Ti, Al)N, TiC coatings deposited by varying the substrate temperature, plasma power density, excitation mode, and titanium to aluminum ratio in the gas phase were investigated. They showed at substrate temperatures up to 700°C and gas

mixture ratios of Ti/Al=0.3-0.5 using the uni-polar pulsed d.c. method, (Ti,Al)N coatings with vast composition could be created. At constant gas phase ratios and plasma parameters an increased substrate temperature resulted in increased titanium content. For the bi-polar d.c. excitation mode higher AlCl$_3$ concentration had to be used in order to obtain the same composition as for the uni-polar case. Besides the cubic (Ti,Al)N phase, hexagonal AlN was found in samples prepared at 700°C and 4 mbar by XRD measurements. The crystallite size of the (Ti,Al)N coatings deposited by uni-polar and bi-polar activation were estimated to be approximately 10 nm. The hardness HV [0.02] was found to be in the range of 25-30 GPa for Ti$_{1-x}$Al $_x$N, up to 32 GPa for TiN, and up to 40 GPa for TiC.

To improve the adhesion behavior of TiN coatings deposited on H13 steel, a layered composite structure had been developed by plasma nitriding and PACVD in the study of Ma et al. [43]. Effects of the nitriding process on the micro-structure, adhesion and micro-hardness, as well as the residual stress of composite nitrided H13/TiN coatings were investigated. Results showed that the adhesion of TiN coatings to substrates could be remarkably enhanced by an optimized plasma nitriding process conducted at a 25% flow ratio of N$_2$/(H$_2$+N$_2$) for 1 h. The formation of a new compound layer during a nitriding process at a 50% flow ratio of N$_2$/(H$_2$+N$_2$).

The adhesion of TiN coatings decreased due to premature brittle fracture between the coating and substrate. The surface hardness of nitrided H13/TiN coatings and the compressive residual stress in the diffusion interlayer increased with increasing pre-nitriding time, but the adhesion of layers reduced to some extent.

TiN films with chlorine content of 1.2–4.9 at.% was prepared on high-speed tool steel substrates at temperatures of 480, 550 and 600°C by Kawata et al. [44]. They investigated structural and tribological properties of films, as chlorine content varied. The chlorine content decreased when the deposition temperature increased. The hardness was changed in the range of 2070–2360 Hv (0.05 N). The friction coefficients and wear factors of films reduced with increasing the chlorine content.

The aim of the study of E. Badisch et al. [43-45] was to use the PACVD technique to create different TiN coatings. Chlorine contents was changed to investigate the tribological properties of coatings at different temperatures and in the range from 25 to 150°C. To investigate the geometry of wear tracks in ball-on-disc testing, an optical 3d profiler was used. Low friction coefficients of 0.14-0.17 gained at the room temperature for coatings that had more than 3 at.% chlorine. The friction coefficient increased to 0.7–0.8 when the ball-bearing steel was used. For testing in dry nitrogen atmosphere, the friction coefficient increased to the

same range [45]. The lowest wear coefficient was observed as Al$_2$O$_3$ ball was applied at the room temperature [46]. Iron oxide layers of a thickness in the nm-range found on low-chlorine containing TiN coatings (3 at.%Cl) showing friction coefficients of approximately 0.8, whereas on TiN coatings with higher chlorine contents (3 at.% Cl) rutile layers were preferably formed, resulting in friction coefficients below 0.2. The self-lubrication mechanism explained by the in-situ formation of titanium oxides in the contact zone in the presence of humidity and oxygen [47].

M. Stoiber et al. [48] deposited TiN coatings. To optimize the friction coefficient and wear properties, chlorine contents changed. Hardness measurements with a nano-indenter was done. Hardness value was about 17.9-24.8 GPa for TiN coatings. Low friction coefficients were in the range of 0.17- 0.22 for those TiN coatings having a chlorine content of 3.2-6.3 at.%.

Prior to TiN depositions, different gases including hydrogen, nitrogen and argon were used for the cleaning and nitriding of cold-working, high chromium tool steel. The aim of this paper was improving adhesion of the TiN films. This was the study of Gammer et al. [49]. Good adhesion was achieved when nitrogen–hydrogen atmosphere with 40%−80% nitrogen was used; the best adhesion quality values were achieved with 40% nitrogen. In contrast to the Argon addition, when higher or lower fractions of nitrogen in the prior gas was present, the films adhesion reduced.

In the research of Son et al. [50], a new simulation of the PACVD coating process for low-temperature deposition of TiN layers was done. They used Tetrakis (dimethylamino) titanium in a pilot plant as an intermediate step in order to apply results for different size of chambers. The deposition depended on the process parameters such as flow rate, pressure, heating temperature, and process gas compositions.

Researchers [51-53] studied effects of surface characteristics and the duty cycle on the corrosion behavior TiN films. When duty cycles increased, rougher surfaces with large size of grain was created. The thickness of layers was about 1.6–2.3 μm. When duty cycles reduced, the hardness of 1723 HV$_{0.05}$ was reported. The results showed that corrosion resistance increased 10 times when the process temperature decreased.

c) Single Coatings: Ti(C, N)   For the first time, Taguchi method was applied to identify the effect of wear-resistant TiCN coating variables on the wear resistance by Wang et al. [54]. They optimized the process temperature and the gas flow rates of a TiCN coating. In this way, better load-carrying capacity was gained, and as a result an improvement in the wear resistance with respect to TiN and TiC coatings was observed.

In the study of Pfohl et al. [55], TiCN coatings were deposited by pulsed d.c. PACVD using either a Cl-containing or an organo-metallic metal donor. Stoichiometric TiN was electrochemically stable in most electrolytes. They claimed that if the formation of micro-pores was not suppressed by the optimal choice of deposition parameters, the low alloyed steel substrate corroded, causing a detachment of the coating. On layers deposited on stainless steel, no sign of substrate corrosion could be detected. High Cl-containing TiC coatings still exhibited an excellent corrosion resistance.

Different TiCN coatings were produced by Dorfel et al. [56]. With increasing carbon content, different texture such as equiaxed grain structure, fan-like structure and very fine columnar structure texture were observed. Most coatings had a mono-phase cubic TiN or TiC structure; except in inter columnar regions for the case whenthe highest carbon content was composed of TiC columns and a graphite-like constituent.

The deposition of TiCN and ZrCN layers on light metals (Al, Mg) by pulsed d.c. PACVD technique using metallo-organic compounds of the type tetrakis (diethyl)-aminometal $(Me(N(C_2H_5)_2)_4)$ was investigated by Rie et al. [57]. The deposition temperature was below 180°C. Hard and adherent layers were deposited on aluminum and magnesium alloys. The growth rate of ZrCN was more than twice that of TiCN. The TiCN and ZrCN layers reached hardness values of up to 1530 HK0.01 and 1400 HK0.01, respectively. The growth rate of TiCN layers correlated with the intensity of Ti^+ in the plasma.

TiCN films were created on an aluminum alloy by using different precursors such as diethylaminotitanium, hydrogen and nitrogen. This was done with the pulsed D.C. PACVD process by Kim et al. [58]. Process parameters like the precursor evaporation temperature, duty ratio, frequency, voltage, H_2/N_2 gas ratio were variables and effects of them on properties of the ceramic layer was investigated. Layers showed high hardness and a low friction coefficient.

In the work of Ma et al. [12], plasma nitriding prior to TiCN coatings was developedusing pulsed D.C. PACVD. Results indicated that the plasma nitriding of AISI H13 steels could improve surface micro-hardness and wear life time of the composite layer.

TiBN and TiCN coatings with and without the plasma nitriding prior to deposit coatings were deposited by He et al. [59]. A radio frequency glow discharge optical emission spectroscope (rf-GDOES) was used for compositional analysis. Results showed that with increasing load, coatings on the substrate with and without prior nitriding deteriorated in the same failure modes. With the prior plasma nitriding, the cohesion and adhesion properties of both coatings were increased. This improvement was related to a gradient hardness architecture.

Podgornik et al. [60] studied 12 types of TiCN-coatings on high-speed steel with vacuum heat treatments to study heat treatment effects on the mechanical, tribological and load-carrying properties of samples. Their results showed that plasma nitriding, simultaneously improves mechanical, tribological and load-carrying properties of tool steel.

d) Multilayer Coatings   Coatings of TiC, TiN and Ti(C,N) by a d.c. PACVD was described by Akchek et al. [61] in 1981. Their results showed that deposition rates had an insignificant effect on the substrate temperature, but the substrate temperature had outstanding effects on coating characteristics. Coatings deposited at temperatures above 400°C for TiN and 500°C for TiC coatings. The rate of deposition was about l-3 $\mu m.h^{-1}$ in experiments and was independent of the substrate temperature.

In the study of S. J. Bull et al. [62], effects of titanium interlayer on the adhesion of titanium nitride deposited by PACVD investigated. They said, as observed for PVD coatings, the critical load for coating detachment increased with increasing interlayer thickness but in contrast with PVD coatings no maximum was observed over the range of interlayer thicknesses investigated. In PVD coatings the titanium interlayer had a significant guttering effect as shown by secondary ion mass spectrometry (SIMS) depth profiles; however, in PACVD coatings, owing to the more effective pre-cleaning stage, improved adhesion with increasing interlayer thickness was attributed more to its compliance.

Thermal and PACVD processes were investigated in the paper of Täschner et al. [63]. The total pressure of the reactor was fixed at 0.5 kPa (4 Torr) with pulsed D.C. voltage (maximum 600V). The range of temperature was about 430-580ºC. The organo-metallic precursors used were (tetrakis (diethylamido)- titanium (TET), tetrakis (dimethylamido)-titanium (TMT), tetrakis (diethylamido). They showed that micro-hardness of layers did not reach the values of comparable conventional CVD or PACVD layers. In all cases the layers contained variable amounts of oxygen impurities.

In the study of Rie et al. [64], layer systems of TiN/Ti(C,N)/TiC were deposited on cermet and steel substrates. Various micro-structures were found for the investigated single layers in the layer systems. All deposited layer systems had a preferred orientation in the (200) direction. Chlorine contents of 0.9, 1.5 and 3.7 at.% were obtained for the TiC, Ti(C,N) and TiN layers respectively. Hardness values of up to 4100 HK0.01 could be obtained for layer systems with TiC at the top. The hardness of the system was dependent on the top layer. The highest values of adhesion were obtained for Ti(C,N)/TiN layers.

A single layer of TiC with a smooth surface and high hardness (about 3000 HK0.01) was formed at 650°C and 650 V by Park et al. [65]. The layer was adhesive to substrates by the formation of chromium carbides at the interface. A single layer of TiN displaying high hardness (about 2400 HK0.01) was formed on the substrate by 550 V. No brittle compound was formed at the interface.

A multilayer of TiN–TiC had been deposited on used die steels by the pulsed d.c. PACVD process by Kim et al. [66]. The TiC layer was deposited at 580°C with a gas mixture of $TiCl_4$, CH_4, H_2 and Ar. A gas volume ratio of $TiCl_4/CH_4$ in the range 0.34-0.38 was required to obtain dense TiC films with minimum excess carbon phases and low chlorine content of less than 2.5 at.%. They used Ratherford backscatter spectroscopy (RBS) for their report.

TiN single coating and TiN/Ti(C,N) multilayer coatings were deposited on the $Cr_{12}MoV$ substrate by PACVD process; which was define by Sheng-Li et al. [67]. The results showed that TiN/ Ti(C,N) multilayer coatings were fine and had free columnar structure. When the process parameters were optimized, hardness and indentation adhesion of TiN/ Ti(C,N) multilayer coatings were better than the TiN single coating. The XRD result showed that the TiN/ Ti(C,N) multilayer coatings had FCC crystalline structure. TiC–TiN gradient films were deposited on silicon substrates by Takahashi et al. [69]. The temperature was about 800°C and titanium tetra-ethoxide solutions stabilized with tri-ethanol amine was injected into thermal $Ar/N_2/H_2$ plasma. TiC–TiN multilayer coatings with different content of C and N atoms were created in this paper as the N_2 flow rate was changed from 0 to 500 ml/min. The SEM images showed that thickness of layers were about 0.7 μm. The particle size range was about 100-500 nm due to the increasing flow rate.

TiC, TiN and TiCN thin films deposited on Si wafer substrates all were demonstrated by Fang et al. [70]. The contact stress–strain relationships and fractal dimension were examined. Results showed that the TiC layers had lower friction coefficient and surface roughness and higher hardness and Young's modulus comparing with the TiN and the TiCN layers. As the indentation depth increased with tips of AFM the Young's modulus and the hardness was reduced for all layers. Hardness values for TiC, TiCN and TiN films ranged from 20.56 to 23.64 GPa, 11.84 to 14.09 GPa and 8.24 to 11.02 GPa, respectively; their Young's moduli ranged from 264.81 to 272.06 GPa, 182.83 to 199.28 GPa and 170.34 to 180.25 GPa, respectively. In Figure 2, AFM images of coatings were observed and showed the TiC film exhibited lower surface roughness.

Composite layers, which consist of TiC and hard amorphous carbon (a-C) were prepared by PACVD by Liepack et al. [22]. XPS and EELS measurements showed that the carbon present in the layer was in the form of sp3 hybridized (70%). As-prepared pure carbon layers were nearly stress relaxed as demonstrated by use of the substrate curvature method. The hydrogen content in the carbon phase was measured to be 8–10 at.%.

Azadi et al. studied [2, 11, 38, 68], mechanical properties of multilayer coatings of TiN/TiC. Substrates in these studies were AISIH13 hot work tool steel. Multilayer coatings that had 10 layers, had the decreased friction coefficient (as 0.2), the highest wear resistance and the toughness (17.7 MPa·m$^{1/2}$) [11]. Mechanical properties such as hardness, wear resistance and surface roughness were changed when the material type of layers in coatings was variable (Figure 3). The TiN/TiC coatings showed the maximum micro-hardness (>27 GPa) and had a better wear resistance than the single-layer coatings. Lower surface roughness was also related to the TiC coating (Figure 2) [2, 68]. When more layers were used in multilayer coatings, the elastic modulus and hardness were increased, too.
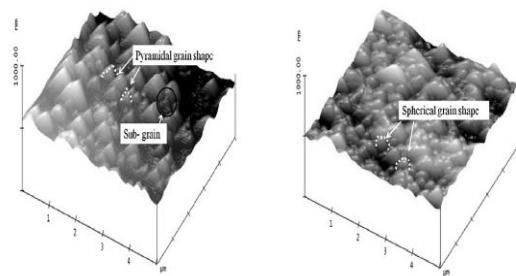
Figure 2. AFM images of (right) TiC, (left) TiN thin films [68]
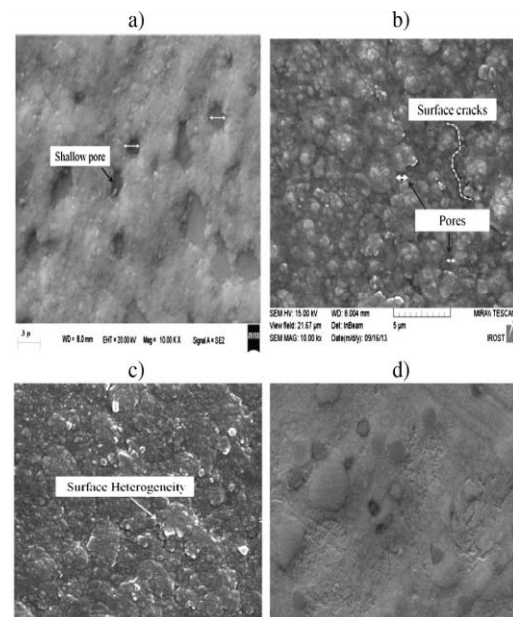
Figure 3. SE images of surface of samples, including: (a) multilayer coatings of 2 layers, (b) multilayer coatings of 4 layers, (c) multilayer coatings of 6 layers and (d) multilayer coatings of 10 layers [11]

The nest mechanical properties such as the elastic modulus and the scratch resistance were related to multilayer coatings with 10 layers [68].

2. SUMMARY

This paper reviewed researches about TiN, TiC and Ti(C,N) (single and multilayer coatings) by PACVD. The main notes including:

1- The deposition of hard coatings such as the TiN and TiC by PACVD provided depositing homogeneous pinhole-free coatings on different substrates with complex shapes.

2- Multilayer depositions produced a fine-grained layer structure, in comparison with single layers, which mostly revealed a coarse-grained columnar structure. XRD revealed the (200) plane as a stable plane for the TiN and TiC by means of PACVD.

3- TiC single coatings had small grain size (<10 nm) when deposited by PACVD and formed by gas precursor. Best mechanical properties such as high hardness (27GPa), wear resistance, fracture toughness and low surface roughness belonged to the coating deposited at 450°C. The TiC layers showed lower surface roughness than TiN and the TiCN layers.

4- Micro-hardness of these coatings depended on the gas phase composition, but no change in structure and texture was observed by variation of precursor source. In addition, duty cycles not only affected the structure and morphology of coatings, but also influenced electrochemical properties.

5- The challenge in TiN coatings was to decrease the chlorine and other impurities in the deposited layers as it caused a decrease in mechanical hardness and wear resistance.

6- In multilayer coatings, the layer stress decreased by about 50% with respect to the single coatings, which resulted in an increase in the layer adhesion. In addition, the corrosion resistance of multilayer coatings was better than single layer coatings.

7- The coatings adhesion with pre-treatment of the substrate was improved compared with that without pre-treatment for all coatings.

8-Optimizing the coating parameters of Ti(C,N) coatings could lead to increase in the wear resistance. Pre-treatment of the substrates were also improved compared with that without pre-treatment for all coatings.

9- Even a small amount of alloying elements like Al or Si addition to TiN coatings had large effects on the improvement in hardness, oxidation resistance and micro-structure of TiN films.

We compared some of mechanical properties such as hardness and friction coefficient of different coatings that were reported by different researchers in Table 1 and Table 2.

TABLE 1. The Hardness (VHN) of different coatings

TiN- TiC	TiN	TiC	T(°C)	Reference
-	-	3200	580	[66]
3150	2100	3000	450	[2]
-	2400	3000	650	[65]
4100	-	-	530	[22]
-	2000	-	400	[29]
-	2100	-	480	[44]

TABLE 2. Friction coefficients of different coatings

TiN- TiC	TiN	TiC	Ref.
0.10-0.35	0.40-0.50	0.10-0.15	[2]
-	0.40-0.50	-	[23]
-	-	0.10-0.30	[15]
-	-	0.18	[18]

In all, there were plenty of researches that investigated the relation of varying process parameters with mechanical, physical and structural properties of these hard coating. But, there is a lack of research on details of the nature and treatment of the plasma in this deposition process. Plasma parameters such as ion and electron fluxes, the plasma formation rate and the plasma type may influence the coating formation and properties. These parameters need further studies.

3. CONCLUSION AND FUTURE DESIGN

During the past three decades, vacuum-based and plasma-based technologies for functional coatings have evolved significantly. Numerous PACVD concepts are industrially applied for optical, protective, biomedical, and other applications. In each work, latest advances in understanding the deposition processes and improved process control led to better film performance. This clearly gave rise to continuously increased acceptance of PACVD technologies in industry.

Current trends point toward the understanding of the physic of the plasma to improve deposition approaches and coatings properties and to control the growth rate of the films. The focusing note also is on the creating nanostructured coatings for various new products in industrial scale.

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A Review on Titanium Nitride and Titanium Carbide Single and Multilayer Coatings Deposited by Plasma Assisted Chemical Vapor Deposition

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چکیده

در این مقاله مروری بر پوشش‌های تک‌لایه و چندلایه نیتریدتیتانیم و کاربیدتیتانیم انجام شده است. این پوشش‌ها از روش ترسیب شیمیایی از فاز بخار به کمک پلاسما ایجاد شده‌اند. تکنولوژی‌های وابسته به پلاسما برای ساخت لایه و پوشش-های نازک در کاربرد گسترده همانند قطعات خودرو و هواپیما، ابزار دیسک کامپیوتر، صنعت غذایی و ابزار پزشکی/ دارویی استفاده می‌شوند. در اینجا به اثر روش ترسیب شیمیایی از فاز بخار به کمک پلاسما به وسیله توصیف عملکرد سیستم‌های متفاوت پوشش‌ها و لایه‌های نازک مناسب برای کاربردهای آزمایشگاهی تا صنعتی پرداخته می‌شود. خواص مکانیکی این پوشش‌ها مانند مقاومت در برابر سایش، سختی، چقرمگی، خواص ساختاری ، فیزیکی و شیمیایی مانند چسبندگی پوشش‌ها به انواع زیرلایه‌ها، رفتار شوندگی و مقاومت در برابر خوردگی مورد مطالعه قرار گرفته است. بنابراین، این مقاله منبع اطلاعاتی خوبی برای کسانی است که قصد آشنایی با دانش در این زمینه از علم و خواص عملکردی مواد، خصوصاً پوشش نیتریدتیتانیم و کاربیدتیتانیم با روش ذکرشده را دارند.

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