TITANIUM-BASED THIN FILMS DEPOSITED BY PVD PROCESSES: A BRIEF REVIEW

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ABSTRACT

This article provides a brief review of titanium-based thin films deposited using physical vapor deposition (PVD) processes on various types of substrates, and also contains a topic dedicated to the deposition of these films using the cathodic cage plasma deposition (CCPD) technique. Thin films play a crucial role in a variety of industrial applications, including corrosion protection, wear resistance and biomedical applications. Titanium is a widely used material due to its excellent corrosion resistance, high hardness and biocompatibility. PVD methods stand out due to the high deposition rate, lower temperatures and treatment times compared to chemical vapor deposition (CVD) processes and have been commonly adopted to deposit titanium thin films on various types of substrates due to their ability to produce high quality coatings with good adhesion and uniformity. The fundamental principles of the cathodic cage plasma deposition PVD process and a review, over *the last five years, of the main research articles in the PubMed, SciELO, ScienceDirect, Scopus and Springer Link databases, highlighting the main deposition parameters, deposition technique used, results and applications of titanium-based thin films deposited on various types of materials are covered in this article.*

KEYWORDS: *Thin films; PVD; Titanium; Deposition.*

I. INTRODUCTION

Within the field of surface engineering, titanium-based thin films stand out due to their remarkable properties such as high hardness, wear resistance, corrosion resistance, antibacterial properties and biocompatibility [1], [2]. Thin films of titanium nitride (TiN), for example, are commonly deposited as coatings on metallic materials to improve surface properties in terms of gaining hardness, resistance to wear and corrosion [3], [4]. Thin films of titanium carbide (TiC) are generally used in coatings of titanium alloys, such as the Ti6Al4V alloy, to improve surface roughness properties and reduce the coefficient of friction [5], [6], [7]. Another class of titanium-based coatings is the thin film of titanium dioxide (TiO_2), which can be present in three crystalline forms (anatase, rutile and brookite) and is usually used as a coating to improve photocatalytic, photodegradation, electrochemical and biological properties [8], [9], [10].

These thin films can be deposited using various techniques based on physical vapor deposition (PVD), such as magnetron sputtering [11], electron-beam evaporation [12], cathodic cage plasma deposition [13], among others, and by chemical vapor deposition (CVD) techniques such as MO-CVD (Metal Organic Chemical Vapor Deposition) [14] and PE-CVD (Plasma-enhanced Chemical Vapor Deposition) [15]. In industrial terms, PVD processes are more popular than CVD due to their higher deposition rate, lower temperatures and treatment times, greater versatility and control of thin film deposition parameters. [16], [17].

Among the various existing PVD techniques, the Cathodic Cage Plasma Deposition (CCPD) technique stands out for its ability to obtain uniform thin films with good adhesion to the substrate and properties that can be controlled by adjusting the deposition parameters [13], [18]. Furthermore, using this technique it is possible, with the right combination of cathodic cage materials and the gas mixture (Ar, H_2, N_2, O_2), to efficiently obtain titanium-based thin films such as nitrides, carbides and oxides, which can be deposited on various types of substrates, from conductive to insulating materials [19], [20].

This paper briefly discusses the fundamental principles of the cathodic cage plasma deposition PVD process and a review of the main research articles in the PubMed, SciELO, ScienceDirect, Scopus and Springer Link databases over the last five years, highlighting the main deposition parameters, deposition technique used, results and applications of titanium-based thin films deposited on various types of substrates.

II. CATHODIC CAGE PLASMA DEPOSITION TECHNIQUE

Almost 20 years ago, the Cathodic Cage Plasma Deposition (CCPD) technique was developed and registered under patent number PI0603213-3. Initially, the work carried out used the same material as the substrate to be treated as the cathodic cage material, and this process was called cathodic cage plasma nitriding [21]. Subsequently, the method was used to deposit films of elements other than those of the substrate to be coated, by changing the material of the cathodic cage, thus being called cathodic cage plasma deposition [22].

A schematic of the CCPD technique can be seen in Figure 1. In this technique, the sample remains isolated (in floating potential) on a disc of insulating material while the cage is cathodically polarized on the sample holder. The process takes place inside a reactor (vacuum chamber) which is anodically polarized. Initially, the plasma is generated, which is formed under specific conditions of pressure, temperature and gaseous atmosphere in the presence of a potential difference. From this point, the sputtering mechanism, which consists of the bombardment of ions/electrons present in the plasma, starts to act on the surface of the cathodic cage, causing the ejection of atoms from the cage material, which in turn combine with the plasma's reactive atmosphere and are deposited on the substrate in the form of a thin film.

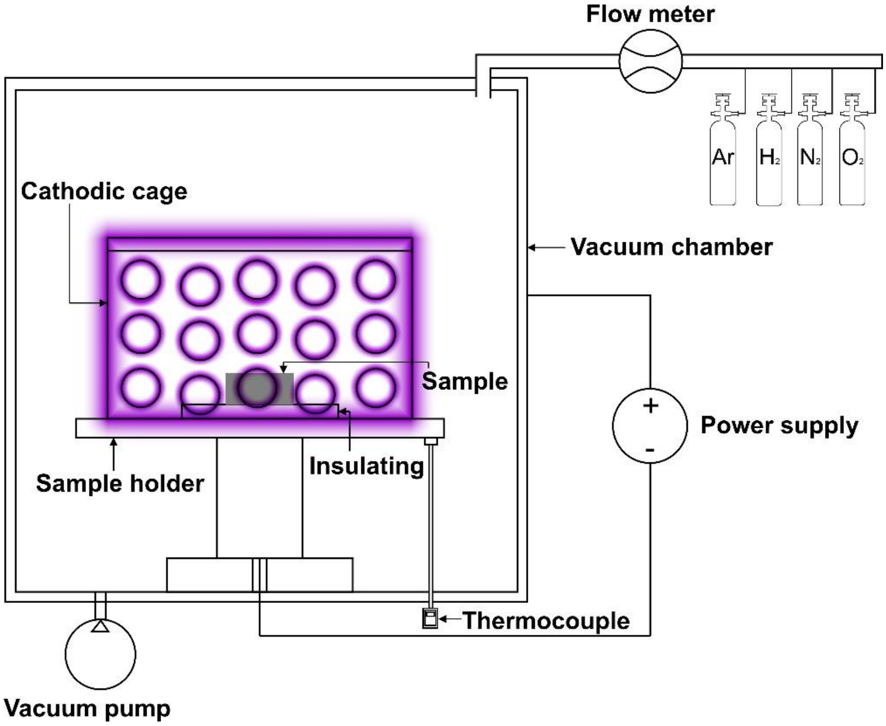

Figure 1 - Schematic of the cathodic cage plasma deposition (CCPD) process.

The advantages of the CCPD technique include the deposition of thin films with greater uniformity, elimination of the edge effect (which causes loss of uniformity and a decrease in hardness in the edge region) related to conventional plasma nitriding treatments, lower temperatures and treatment times compared to conventional plasma deposition methods, improved adhesion of the film to the substrate, the possibility of controlling treatment parameters to adjust properties, good reproducibility of treatments, the possibility of application on conductive and insulating substrates, among others [19]. In situations where surface roughness is considered an important property and must be kept at low levels, the CCPD technique is not recommended due to the nature of the ion bombardment caused during sputtering, which causes surface erosion with a consequent increase in roughness [23].

III. TITANIUM-BASED THIN FILMS

Thin titanium-based films such as TiN, TiC, TiO_2, titanium itself, among others, have several interesting properties that give them outstanding commercial and technological importance, such as: high hardness, resistance to wear and corrosion, biocompatibility, among others [24]. The search for research articles published in the last five years was carried out by consulting the PubMed, SciELO, ScienceDirect, Scopus and Springer Link databases from March to April 2024, based on the following keywords: Titanium thin film and physical vapor deposition or PVD. This search did not take into account articles that used the cathodic cage plasma deposition technique to obtain the films. The inclusion criteria for choosing the articles were based on the following parameters: i) research articles; ii) published in the last five years (from 2019); iii) films deposited using the PVD technique; iv) titanium-based films. The exclusion criteria used were: i) review articles; ii) articles published before 2019; iii) articles that used the cathodic cage plasma deposition technique to obtain thin films. Based on this information, the initial search provided the following numbers of research articles in their respective databases: PubMed (9), SciELO (7), Science Direct (13), Scopus (2) and Springer Link (1).

After a detailed analysis of the research articles obtained and considering the inclusion/exclusion criteria and removal of duplicates, 15 articles were selected for analysis which are listed in Table 1 in terms of the type of thin film deposited, substrate and deposition technique.

Single-phase Ti films are widely used as coatings to improve adhesion, roughness, corrosion and biological properties, among others. In this sense, Suliali et al., (2022) [25] deposited thin Ti films on FTO (Fluorine-doped Tin Oxide) glass substrates using the magnetron sputtering technique (high power pulse) to evaluate the influence on surface roughness. The authors observed a non-linear dependence of surface roughness in relation to the power applied to the Ti target, where it was observed that the best power to be used to obtain the lowest surface roughness (14 nm) was 4.50 kW. Sabavath et al., (2022) [26] used the magnetron sputtering technique to deposit Ti thin films on silicon substrates in order to evaluate the influence of the plasma parameters (temperature and electron density) and the deposition rate on the thickness of the deposited thin film. The distribution of the magnetic field created during the treatment strongly influenced the plasma parameters and the deposition rate, where increasing the axial and radial distance from the cathode led to a decrease in layer thickness and deposition rate.

Table 1 - Articles on titanium-based thin films deposited by PVD processes.

Thin film	Substrate	Deposition technique	Reference
Ti	FTO glass	*Magnetron Sputtering*	[25]
Ti-O-N, Ti-Cu-N	Glass	*Cathodic arc evaporation, Magnetron Sputtering*	[27]
TiO_2	SiO_2/Si	*Magnetron sputtering*	[28]
Ti, V	FTO glass	*Magnetron sputtering*	[29]
Ti	Si, glass	*Magnetron sputtering*	[30]
Al-Ti, Cu-Ti, Ag-Ti, Au-Ti	Si	*Magnetron sputtering*	[31]
Ti	Si, NaCl, sapphire	*E-beam evaporation*	[32]
Ti, Al_2O_3/Ti	316LSS	*Magnetron sputtering*	[33]
TiO_2:ZnO/CuO	Si, ITO	*Magnetron sputtering*	[34]
TiCu	PET, Si	*Magnetron sputtering*	[35]
TiNi	SiN, SiN/Cr	*Magnetron Sputtering*	[36]
Ti-Cu-Ag	Si	*Magnetron Sputtering*	[37]
TiO_2	p-Si	*E-beam evaporation*	[12]
Cu-TiO_2	Glass	*Magnetron sputtering*	[38]
Ti	Si	*Magnetron sputtering*	[26]

Also, with regard to single-phase Ti, Zgheib et al., (2021) [30] coated silicon and glass substrates with thin Ti films using the magnetron sputtering technique with the samples fixed at different angles (0º, 45º and 80º) to determine the elastic constants of the films and evaluate their morphology and crystalline structure. The porous microstructure with columnar growth obtained with the deposition of the films suffered inclinations in the direction of the vapor flow as the angle of incidence increased. Increasing the angle of incidence led to a decrease in the hardness and modulus of elasticity and shear of the films, which was attributed to the presence of porosity in the film structure. Devulapalli et al., (2021) [32] evaluated the influence of substrate types (Si, NaCl and sapphire) and deposition parameters on the microstructure of Ti thin films deposited using the Electron Beam Evaporation technique. The deposited films exhibited a nanocrystalline structure regardless of the type of substrate. Parameters such as strain energy and surface energy directly influenced the type of crystalline orientation of the films, which had an impact on the resistivity of the films to favor their application in the microelectronics industry. Increasing the deposition rate resulted in a smaller grain size in the nanocrystalline structure of the films.

Peri, Bhagavathiachari and Balasubramanian (2022) [29] deposited thin films based on Ti and V, as well as binary and ternary nitrides and carbides, on FTO glass substrates using the magnetron sputtering technique with the aim of evaluating the electrochemical properties of the films (as a coating on electrodes) for use in energy conversion and storage. All the films showed energy storage characteristics (application in solar cells and supercapacitors), with the V-based films showing the highest energy conversion efficiency as a counter electrode and the electrodes coated with Ti-based films demonstrating a high potential window. All the electrodes coated with ternary films proved to be operational even at higher currents, maintaining stability.

Abd El-Fattah et al., (2024) [33] studied the corrosion characteristics of thin Ti and Al_2O_3/Ti films deposited on 316LSS steel using the magnetron sputtering technique, with one group of these films undergoing normalization heat treatment and the other undergoing annealing. The authors observed that the Ti films, as deposited, showed better corrosion resistance than the Al_2O_3/Ti films, while after the annealing treatment, the Al_2O_3/Ti thin films showed better corrosion resistance and a lower corrosion rate as a result of the formation of a homogeneous iron oxide layer on the surface.

Coatings based on titanium dioxide (TiO_2) have various properties of interest, such as use in photocatalysis, photodegradation, photovoltaic cells, electrochemical sensors, biological applications, among others. In this context, Graillot-Vuillecot et al., (2022) [28] investigated the structural, morphological and optical properties of TiO_2 thin films deposited on SiO_2/Si and sapphire substrates by magnetron sputtering using two configurations of Ti targets, one heated and one unheated (conventional). The authors observed that the use of heated targets allowed the growth of a single crystalline anatase phase, while the films obtained with the unheated target exhibited a mixture of anatase and rutile phases with low crystallinity. In addition, the best optical transparency was observed in the film deposited using the heated configuration and optical bandgap values of 3.27 eV were achieved for this type of film, which is close to those obtained conventionally. Model et al., (2022) [12] evaluated the influence of the thickness of TiO_2 thin films deposited by electron beam evaporation (ranging from 50 nm to 90 nm) on the reflectance and surface passivation of silicon solar cells. It was observed that thicker films improve surface passivation and that the film thickness that provided the lowest reflectance and the most efficient solar cells was 80 nm.

An alternative way of improving the properties of TiO_2 films is by combining or doping them with other materials. Wisz et al., (2022) [34] analyzed the structural, morphological and optical properties of TiO_2:ZnO/CuO thin films for application in solar cells. The films were deposited on Si and ITO (indium/tin oxide) substrates using the magnetron sputtering technique. The films exhibited a columnar grain morphology which is desirable for a photovoltaic thin film. The TiO_2 films with a ZnO layer (TiO_2:ZnO) showed lower values of photovoltaic parameters compared to the pure TiO_2 film, which may be related to obtaining a more amorphous structure that directly affects the efficiency of the photovoltaic parameters. In another study, Moretti et al., (2021) [38] deposited thin TiO_2 films doped with copper in order to evaluate their photocatalytic properties. The thin films were deposited using the magnetron sputtering technique and then underwent annealing heat treatment at 600 ºC in different atmospheres (Ar, O_2, H_2). The copper-doped TiO_2 films (Cu-TiO_2) exhibited greater photocatalytic activity than the pure TiO_2 film treated in an H_2 atmosphere.

Ferreira et al., (2022) [35] analyzed the antibacterial and piezoresistive properties of TiCu thin films, with copper as the doping agent, deposited on Si and PET substrates in order to apply this coating to high-traffic surfaces such as elevator buttons, light switches, door handles, among others, in order to prevent bacterial and viral infections. With the deposition of the films, the authors observed an increase in antimicrobial activity with increasing Cu content, reaching the best behavior with 63 at.% Cu. In addition, the films showed an increase in piezoresistive sensitivity, improving the electromechanical response with the ability to detect touch, force and deformation.

Rashid et al., (2021) [37] deposited Ti-Cu-Ag thin films by magnetron sputtering on Si substrates and analyzed the influence of Ag content on the mechanical properties of the thin films. Films containing up to 25 at.% Ag exhibited the best balance between modulus of elasticity and hardness while maintaining the potential to increase antibacterial properties, and could be used as a coating to improve the biomedical properties of implants.

Dang et al., (2021) [36] evaluated the mechanical properties of TiNi thin films deposited on two types of substrate, SiN-coated silicon and SiN/Cr-coated silicon using magnetron sputtering. The highest elastic modulus values as well as the lowest residual stress were identified by the TiNi film deposited on the substrate containing the Cr interlayer. The presence of Cr at the interface acts as a damping layer that prevents deformation due to the intermediate values of the coefficient of thermal expansion between the substrate and the film, which contributes to the increase in fatigue resistance with this type of substrate.

Lopes et al., (2020) [31] analyzed the mechanical properties of Ti thin films doped with different materials (Al, Cu, Ag, Au) deposited on Si substrates using the magnetron sputtering technique. It was observed that the adhesion strength of the film/substrate interface showed better results for the films doped with Au, Cu and Ag and that the surface hardness showed better values for the Ti-Au and TiCu films as well as in terms of toughness, such characteristics were attributed to the metallic "glass-like" thin film microstructure obtained for these two systems, which can be applied in biopotential electrodes for non-invasive physiological monitoring.

Jokanović et al., (2022) [27] combined magnetron sputtering and cathodic arc evaporation PVD processes to deposit titanium oxynitride (Ti-O-N) and copper-doped titanium nitride (Ti-Cu-N) thin films on glass substrates to evaluate the films' physicochemical properties. The Ti-O-N films showed an extinction coefficient, molar absorptivity, close to zero, which makes them exceptional for use as capacitors. On the other hand, the Ti-Cu-N films showed high values of molar absorptivity, typical of materials used in applications that require extremely high reflectance.

3.1. Titanium-based thin films deposition by CCPD

This topic brings together research articles in which the Cathodic Cage Plasma Deposition (CCPD) technique was used to deposit titanium-based thin films on various types of substrates. To carry out this search, only research articles published in the last five years were considered, by consulting the PubMed, SciELO, Science Direct, Scopus and Springer Link databases in terms of the following keywords: Cathodic cage plasma deposition and titanium. The initial search yielded the following number of research articles in their respective databases: PubMed (0), SciELO (3), Science Direct (10), Scopus (2) and Springer Link (5). After a rigorous analysis of the research articles obtained and considering the inclusion/exclusion criteria and removal of duplicates, 15 articles were selected for analysis which are listed in Table 2 in terms of the following parameters: type of thin film deposited, substrate, treatment temperature, treatment time, treatment atmosphere and type of potential. The main results and applications of each article are briefly presented below.

Thin films of titanium nitride (TiN) were deposited by CCPD on different substrates in order to improve mechanical, tribological, optical, thermal and corrosion properties. Barbosa et al., (2021) [39] observed that increasing the treatment time led to an increase in film thickness, microhardness and corrosion resistance. Defects such as voids and cracks, related to conventional plasma techniques, were not observed with the CCPD technique used, which could enhance its use in industrial applications. De Abreu et al., (2022) [40] were able to achieve significant improvements in the surface properties of M2 steel through plasma duplex treatment (nitriding followed by CCPD), where, through the application of the CCPD technique, the greatest increase in microhardness (at 450 ºC) was observed along with a good hardness gradient. A reduction in the wear rate and friction coefficient was also observed through the duplex treatment used, while still maintaining strong adhesion of the film to the substrate. Nascimento et al., (2022) [41] compared the magnetron sputtering (MS) technique with the CCPD technique and observed that thin films with better mechanical properties and greater color variation are obtained by CCPD, while those obtained by MS have a higher stoichiometric degree. Silva et al., (2023) [42] improved the surface properties of UNS S32750 steel by means of plasma duplex treatment (nitriding followed by CCPD), in which it was observed that the application of nitriding alone at 350 ºC showed better results in terms of hardness and corrosion properties than the duplex treatment at the same temperature, but at 450 ºC the subsequent application of the CCPD technique achieved the best results in terms of corrosion resistance. It was also observed that the lowest wear rates and the lowest coefficient of friction were obtained for the treatments carried out using the CCPD technique, regardless of the treatment temperature studied. Cerqueira et al., (2023) [43] compared TiN thin films obtained by hollow cathode and cathode cage arrangements. Thicker, harder and more uniform films were obtained with the hollow cathode, while the CCPD technique obtained the greatest reductions in the contact angle, exhibiting superhydrophilic files which suggests great potential for TiN-coated Ni-Cr alloys in improving osseointeraction and biocompatibility.

Table 2 - Articles on titanium-based thin films deposited using the CCPD technique.

Thin film	Substrate	Treatment temperature	Treatment time	Treatment atmosphere	Type of potential	Reference
TiN	AISI D6	400 °C	0.5 h - 4 h	12 sccm H_2 / 3 sccm N_2	Floating	[39]
TiN	AISI M2	400 - 450 °C	4 h	30 sccm H_2 / 10 sccm N_2	Floating	[40]
TiN	Silicon	300 - 350 °C	2 h - 4 h	25% N_2 / 75% H_2	Floating	[41]
TiN	UNS S32750	350 - 450 °C	2 h	40 sccm H_2 / 20 sccm N_2	Floating	[42]
TiN	Ni-Cr alloy	400 °C	4 h	50% H_2 / 25% Ar / 25% N_2	Floating	[43]
TiN	Glass	400 °C	4 h	Ar and N_2 variation	Floating	[44]
MoS_2-TiN	AISI 1045	430 °C	4 h	80% N_2 / 20% H_2	Cathodic	[45]
MoS_2-TiN	AISI M2	430 °C	4 h	80% N_2 / 20% H_2	Floating	[46]
FeN / TiN	UNS S32760	450 °C	2 h - 4 h	25% H_2 / 75% N_2	Floating	[47]
FeN / TiN	AISI 304	400 °C	4 h	60 sccm N_2 / 15 sccm H_2	Floating Cathodic	[17]
TiC	AISI 420	400 °C	4 h	50 sccm Ar	Floating Cathodic	[48]
Ti–Nb–C–N	AISI 4340	300 - 400 °C	4 h	Variation of H_2 and N_2	Floating	[49]
Ti–Nb–C–N / MoS_2	AISI 4340	300 - 400 °C	4 h	32 sccm H_2 / 8 sccm N_2	Floating	[50]

Madureira et al., (2023) [44] observed that varying the treatment atmosphere influenced the stoichiometry, optical and thermal properties of TiN thin films. It was observed that lower amounts of

N_2 led to more stoichiometric films with higher reflectivity, lower thermal diffusivity and higher electrical conductivity, which proved to be good properties for use as thermal mirrors or thermally regulated coatings.

Silva et al., (2020) [45] applied the CCPD and magnetron sputtering techniques, in that order, to deposit MoS2-TiN films on 1045 steel. In this study, the CCPD technique increased the mechanical strength and adhesion of the multilayer films through the deposition of iron nitrides and TiN, further corroborating the improvement in the wear resistance of the films. The MoS_2-TiN coating showed good characteristics as a solid lubricant with high wear resistance. Similar results were obtained in the work by Libório et al., (2020) [46] who used the same combination of techniques and the same coating deposited in the previous work, but to coat M2 steel.

In the work by De Almeida et al., (2021) [47] the tribological properties of UNS S32760 superduplex stainless steel were improved by depositing TiN and $Fe_{2\text{-}3}N$ films using duplex plasma treatment (nitriding followed by CCPD). Sampaio et al., (2023) [17] used the same duplex plasma treatment on AISI 304 steel and a modification of conventional duplex, simultaneous duplex, in which the sample remains at cathodic potential and nitriding and deposition occur simultaneously. They observed that in addition to improved mechanical properties and wear resistance, the TiN films obtained using the CCPD technique showed better corrosion resistance results when compared to the conventional plasma nitriding technique.

In another study, Naeem et al., (2024) [48] improved hardness, coefficient of friction, wear resistance and corrosion resistance by depositing (at cathodic potential and floating) Ti-C-based thin films on AISI 420 steel substrates. The authors observed a substantial increase in hardness with the deposition of the films at cathodic potential, reaching an average value of 1532 $HV_{0,25}$ compared to 220 $HV_{0,25}$ for untreated steel. The wear volume with the film was reduced from 1200 x 10^{-4} mm^3 to 20 x 10^{-4} mm^3 and the corrosion rate was reduced from 36 x 10^{-6} mm/yr to 6 x 10^{-6} mm/yr. The best results were obtained in the floating potential cathodic cage configuration.

Neto et al., (2023) [49] modified the CCPD technique by inserting targets made of composite materials into the holes in the cathodic cage lid. The ring-shaped targets are made up of 80% TiO_2 + 10% Nb_2O_5 + 10% graphite, in order to produce Ti-Nb-C-N composite thin films. The treatments were carried out at temperatures of 300 ºC, 350 ºC and 400 ºC, and the flow of H_2 was varied, with treatments being carried out with 20, 50 and 80% H_2. The hardness after deposition of the film at 400 ºC and 50% H_2 increased by around 5 times compared to that exhibited by untreated AISI 4340 steel. The wear rate was significantly reduced as the H_2 flow and treatment temperature increased. The study showed that the modification of the CCPD technique proved to be efficient in terms of obtaining films with high hardness and resistance to wear, thus expanding the application of coated 4340 steel for orthopedic joint implant applications. Another study by Neto et al.,(2024) [50] used the same modification of the CCPD technique as the previous work, with the difference of depositing MoS_2 together with the Ti-Nb-C-N film to coat AISI 4340 steel. In this new study, they observed that the introduction of MoS_2 led to a reduction in the coefficient of friction and was considered to be a self-lubricating film with high hardness, which could be used as a coating in applications requiring high wear resistance and self-lubricating performance.

IV. CONCLUSIONS

Several recent studies on titanium-based thin films deposited by different PVD techniques on various types of substrates have been covered in this brief review article. Among the PVD processes, a majority of magnetron sputtering and cathodic cage plasma deposition (CCPD) techniques were observed, sometimes used in isolation or in combination with each other. The prominent use of these techniques can be attributed to their versatility and the possibility of adjusting control parameters in order to improve specific surface properties. The deposition of titanium-based thin films (TiN, TiO_2, TiC, MoS_2-TiN, FeN/TiN, etc.) by means of these techniques is a promising alternative for use as a coating on different substrates, due to the lower temperatures and treatment times, as well as obtaining layers with high performance surface properties exhibiting excellent interfacial adhesion strength between film and substrate, in addition to allowing greater control of the deposition parameters which directly influence the structural, morphological, mechanical, electrical, optical, wear and corrosion resistance and tribological properties. However, little has been reported on the use of these coatings in biomedical applications, which represents a research gap to be explored in more detail and thus contribute to expanding the use of titanium-based thin films obtained by PVD techniques.

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