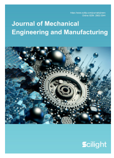
Scilight

Journal of Mechanical Engineering and Manufacturing

https://www.sciltp.com/journals/jmem



Review

Doping Strategies for TiAlN-Based Cutting Tool Coatings: Progress and Perspectives

Gustavo F. Pinto [1,2,*], Francisco J. G. Silva [1,2], Eduardo Silva [3], Naiara P. V. Sebbe [1,4], Ricardo Alexandre [5], Filipe Fernandes [1,6] and Andresa Baptista [1,2]

1 CIDEM, ISEP, Polytechnic of Porto, Rua Dr. António Bernardino de Almeida, 4249-015 Porto, Portugal
2 LAETA-INEGI, Associate Laboratory for Energy, Transports and Aerospace, Rua Dr. Roberto Frias 400, 4200-465 Porto, Portugal
3 Durit Coatings, S.A., Pq. Industrial de Taveiro, 3045-504 Taveiro, Portugal
4 FEUP—Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
5 Inovatools Portugal Unip. Lda, R. da Indústria Metalúrgica 593, 2430-528 Marinha Grande, Portugal
6 Department of Mechanical Engineering, ARISE, CEMMPRE, University of Coimbra, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal
* Correspondence: gflp@isep.ipp.pt; Tel.: +351-228-340-500

How To Cite: Pinto, G.F.; Silva, F.J.G.; Silva, E.; et al. Doping Strategies for TiAlN-Based Cutting Tool Coatings: Progress and Perspectives. *Journal of Mechanical Engineering and Manufacturing* **2026**. https://doi.org/10.53941/jmem.2026.100010

Received: 22 October 2025
Revised: 18 November 2025
Accepted: 1 December 2025
Published: 9 February 2026

Abstract: The continuous technological evolution of industry has intensified the role of machining processes, directly influencing product quality and industrial demands. Research in this field has long focused on friction during machining and the benefits of coatings in reducing energy consumption, improving workpiece quality, and extending tool life. Coated tools have been developed to overcome critical challenges, including thermal stability, corrosion resistance at elevated temperatures, and wear resistance under high speed machining. To meet these requirements, coating technologies have advanced, with methods such as CVD, PVD, and hybrid deposition gaining prominence. However, systematic evaluations of the performance evolution of TiAlN-based coatings doped with additional elements still require some attention from researchers. This review addresses that gap by examining the development of TiAlN coatings doped with elements like Mo, Si, Y, Ta, and Cr, as well as their combinations. It also discusses deposition techniques, thin film technologies, and their influence on coating performance. Finally, the paper outlines current trends, future research opportunities, and open challenges, providing insights relevant to both academy and industry.

Keywords: PVD sputtering; CVD; TiAlN; doping elements; hard coatings; cutting tools

1. Introduction

Machining plays a crucial role in the metalworking industry, which has experienced steady growth and has become an essential part of modern manufacturing. Sousa et al. expect this growth to continue in the coming years [1]. The aerospace and aeronautical sectors demonstrate the demand for complex, high precision parts [2,3]. Advanced 5- and 6-axis machining meets these needs by enabling the efficient production of detailed components while reducing downtime and the number of setups required from raw material to final product [4,5]. Despite the development of new manufacturing processes, the injection moulding industry remains a significant part of production, accounting for over 30% of plastics worldwide [1]. While enabling the large-scale production of high quality products, the industry must continually improve and adapt to market demands to remain competitive [2–4]. Recent efforts have focused on making the process more sustainable and improving product quality, both of which are highly valued in today's industry. Due to strong competition, research has centred on improving processes and materials to enhance performance and energy efficiency [6]. Scientists are working to optimise machining and moulding parameters to reduce production time and costs, increase productivity, and ensure better product quality [7]. Wu et al. [8] emphasise the importance of optimising CNC operations for reducing costs, minimising defects and improving productivity. Current research focuses on improving process efficiency by reducing machining times and increasing tool lifespan through advanced coatings. Siddiqui et al. [9] introduced a self-lubricating textured tool that was tested on an Al6061-T6 alloy, and Dittrich et al. [10] used artificial intelligence and machine learning to automate parameter optimisation. Neural networks are often used to predict tool wear, supported by modern sensors for monitoring and diagnostics [11]. The integration of modern sensors with computational intelligence techniques has enabled the real time monitoring of operating conditions, helping to predict and mitigate of wear [12–14]. Ravikumar et al. [15] states that the growing interest in extending tool lifespan has driven the development of monitoring methods during the machining process. Efforts to extend tool lifespan have also driven advances in real time monitoring and autonomous machining. Genetic algorithms, adaptive fuzzy, and neural networks have been employed to optimise wear tolerance and cutting performance [16]. Studies such as [17,18] show that vibration data and acoustic emission signals, combined with advanced machine learning methods, allow accurate prediction of tool wear. In addition to coating materials, attention must also be given to the deposition process itself. Alongside tool coatings, deposition processes remain relevant. For example, early methods such as electroplating improved wear and corrosion resistance, but posed environmental concerns. Although galvanic processes such as electroplating can achieve the desired coating quality, they have significant environmental drawbacks [19]. They use baths that produce toxic heavy metals, harmful gases and waste, which can lead to severe water pollution from substances such as cyanides and metal ions [20–26]. Consequently, companies are increasingly adopting more sustainable alternative coating technologies, such as Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD), to reduce their environmental impact and eliminate solvent use [27,28]. PVD offers significant advantages: being ecofriendly, requiring low maintenance, and controlling the composition and structure of the films. It provides excellent adhesion, homogeneous layers, and the ability to deposit multi graded systems. Crucially, it operates at low temperatures (350–600 °C), making it ideal for heat sensitive substrates, and has lower overall energy consumption compared to CVD. In contrast, CVD requires much higher temperatures (750–1150 °C), resulting in higher energy consumption, especially concentrated in the heating phase, which is unfavorable in terms of cost and sustainability compared to PVD [29,30].

A detailed understanding of manufacturing techniques is required for the deposition of high performance coatings. This section begins with the fundamentals of PVD and CVD technologies (Section 1.1) and then details the most relevant PVD methods, such as evaporation (Section 1.1.1) and, in particular, sputtering (Section 1.1.2). Sputtering is the main focus of this study.

1.1. Coatings Fundamentals (PVD and CVD)

The first recorded attempts at thin film deposition date back to 1857, when Faraday conducted the first experiment involving the evaporation of metallic wires in a vacuum [31]. In 1887, Nahrwold et al. [32] achieved a significant milestone in the study of Joule heating phenomena, contributing to the understanding of the associated thermal processes. This was followed by Nahrwold's successful reproduction of the process using Joule heating in 1887. The technology was scaled up for industrial use around 1946 after World War II. By 1958, Holland had documented its rapid growth in applications [33]. Although the concept of physical vapour deposition (PVD) dates back to the early 1900s, and a plasma-assisted form was patented over 80 years ago, it only became widely adopted in industry during the 1960s and 1970s [34,35]. PVD technology has continued to evolve, with improvements being made to vacuum, plasma and sputtering techniques, as well as to magnetic fields, thermal evaporation and arc methods. These advancements have enabled PVD films to be applied to a wider range of materials, thereby improving their mechanical properties. Nowadays, PVD remains a field of interest for scientists and industry alike [36]. New materials and techniques are continually being developed for applications in diverse sectors, including aerospace [37,38], electronics [38,39], automotive [40], and even fashion [41]. In the early 1960s, researchers in the USSR, first at the Kharkov Polytechnic Institute and later at the Paton Electric Welding Institute in Kiev, investigated PVD coating processes, producing both thin and thick films using aluminum (Al) and zinc (Zn) on steel substrates [42]. Reviews by Bunshah et al. [43] and Paton et al. [44] highlighted that thin films underwent more extensive development compared to thick films. In 1963, Mattox [45] reported on the ion plating technique, which attracted considerable attention due to its promising results. His work demonstrated that thin films could achieve excellent adhesion, even when the coating and substrate materials were mutually insoluble. According to Mattox [46], the PVD process is based on a deposition mechanism in which coatings grow atom by atom on the substrate. This involves the atomization or vaporization of material from a solid source (the target) within a controlled environment, vacuum, plasma, gaseous, or electrolytic. Vacuum deposition chambers are particularly advantageous, as they minimize gaseous contamination, enable the formation of uniform films with smooth surfaces, and help prevent defects at sharp corners. Crucially, the intrinsic properties of the substrate can significantly influence the characteristics of the resulting thin film.

Following Mattox's pioneering work [45,46], the scientific community has continued to show strong interest in PVD technology, consistently validating and expanding upon his results. Subsequent research has focused on enhancing coating properties, improving deposition rates [47–49], and strengthening adhesion, with particular emphasis on the crucial role of initial surface cleaning to eliminate contaminants and avoid weak or defective coatings [50,51]. Key parameters such as deposition environment, grain size, and deposition rate directly influence coating performance, affecting hardness, Young's modulus, morphology, microstructure, and chemical composition [52].

In recent years, significant progress has been achieved in PVD thin film coating technologies, particularly for nanocomposite transition metal carbide and nitride substrates [53–56]. Among gaseous state PVD techniques, the two most widely used are evaporation and sputtering. In both processes, particles are extracted from a target within a low pressure vacuum or plasma environment, subsequently directed and condensed onto the substrate [57].

Evaporation generally occurs in vacuum conditions with relatively low atomic energy, reducing gas adsorption during deposition. However, this process typically transfers larger grains and results in lower film adhesion compared with sputtering [29]. While evaporation achieves higher deposition rates, it is more suitable for producing thicker coatings with less stringent surface morphology requirements. Conversely, sputtering is favored in applications demanding high morphological precision, including accurate control over surface roughness, stoichiometry, and grain size. Nevertheless, sputtering can induce tensile stress during cooling [58–60]. Despite these limitations, sputtering remains one of the most widely adopted PVD techniques due to its reliability and ability to meet industrial performance requirements [61].

Over the past few decades, PVD deposition technology has been widely adopted for CNC milling and turning tools [62], which demand critical properties such as high temperature hardness, toughness, rigidity, abrasion resistance, and chemical stability [63–68]. PVD coatings provide several advantages, including (a) excellent adhesion; (b) controlled morphology; (c) uniform layer formation; and (d) a broad spectrum of tunable material properties [69–73]. The performance of thin films is strongly influenced by the mechanical characteristics of the substrate and by the property gradient that exists between the coating and the underlying material [74–78]. This technology has also been extensively applied to metallic substrates that require properties such as wear resistance, high hardness [79], corrosion resistance, and low friction [73]. One of the key advantages of PVD is its ability to combine these attributes within a single coating, allowing the performance to be tailored to meet the specific demands of different industrial applications [28,80,81].

As previously described, PVD is a coating technique that allows the deposition of either single layer or multilayer films of target materials onto a substrate, as further detailed in this study. The coating thickness alters the mechanical, tribological, thermal, optical, and electrochemical performance. The effects depend on the type of coating, deposition method, and the substrate [82–84]. Thicker coatings increase wear resistance and extend the lifespan, however, excessive thickness can cause failures due to increased internal stresses [85–87]. Effective hardness results from the combination of substrate and coating, therefore the thickness must be optimized to avoid brittleness or premature fracture. High residual stresses, which increase with thickness, can hinder film adhesion and cause delamination. Furthermore, coatings must be thick enough to provide effective thermal insulation and oxidation resistance, contributing to greater thermal stability and the ability to operate at higher cutting speeds. The balance of thickness influences film efficiency. For example, Arturo et al. [88] studied the main metrics for a thickness on a scale of 1–10 µm and concluded that there was an influence on wear and durability under load. Ponte et al. [89] studied the main metrics affected for a thickness between 2–10 µm and also concluded that there was an influence on the surface hardness obtained, as well as an improvement in edge protection, and greater resistance to tool wear. The resulting coating thickness can range from just a few nanometers to several micrometers, depending on multiple physical parameters of the deposition process. These include chamber pressure, reactive gas composition, target power, temperature, target material, as well as cleaning and deposition times. Each deposition method operates under specific conditions, carefully optimized for both the substrate and the intended performance of the final coating [90]. Although sputtering typically achieves lower deposition rates than evaporation, its quality and deposition efficiency have improved considerably over the years. This progress, combined with its ability to satisfy both industrial and research requirements, has led to its widespread adoption. Moreover, sputtering can be used as an interlayer to improve adhesion between the substrate and the deposited material, or as part of a hybrid approach when combined with other techniques such as chemical vapor deposition (CVD) [91].

CVD, another widely applied vacuum deposition method, relies on chemical reactions to form solid films on a substrate. Similar to sputtering, it can serve as an interlayer to enhance durability, reduce friction, and improve thermal stability. By integrating PVD and CVD layers, it is possible to combine the strengths of both methods, producing coatings with superior mechanical, thermal, and wear resistant properties [91–93]. Advancements in coating analysis techniques, evaluating properties such as adhesion, corrosion resistance, wear resistance, and friction coefficients, have also received considerable attention, with researchers striving to make these assessments more efficient and cost effective [65].

In parallel, the use of numerical simulations and mathematical modeling has grown steadily, serving as valuable tools to optimize deposition parameters and enhance coating performance. Such approaches not only demonstrate the potential to reduce process costs significantly but also contribute to improving the mechanical properties of thin films [94–98].

PVD coatings can be categorized into several types: (a) monolayer; (b) bilayer; (c) multilayer; (d) nanolayer; (e) gradient; and (f) nanocomposite coatings. They may also incorporate specialized alloys with tailored compositions and structures, as will be discussed in detail later [1]. The ability to continuously adjust coating properties across different layers provides remarkable flexibility, enabling adaptation to a wide range of industrial applications [99–104]. This versatility has driven continuous refinement and expansion of deposition techniques, giving rise to numerous variants. Figure 1 provides a structured, hierarchical overview of the main techniques for depositing thin films from the gas phase. This overview is central to materials science and engineering and facilitates an understanding of the complexity and diversity of the coating methods covered. Also allows us to identify the relationships between high-level methodologies, such as PVD (physical vapor deposition), CVD (chemical vapor deposition), and IBAD (ion beam-assisted deposition), and their specific subdivisions, such as evaporative (resistive and e-beam) and sputtering (magnetron, DC, and RF). Among these, sputtering and evaporation remain the most extensively studied and widely applied methods for thin film deposition, owing to their proven reliability and adaptability.

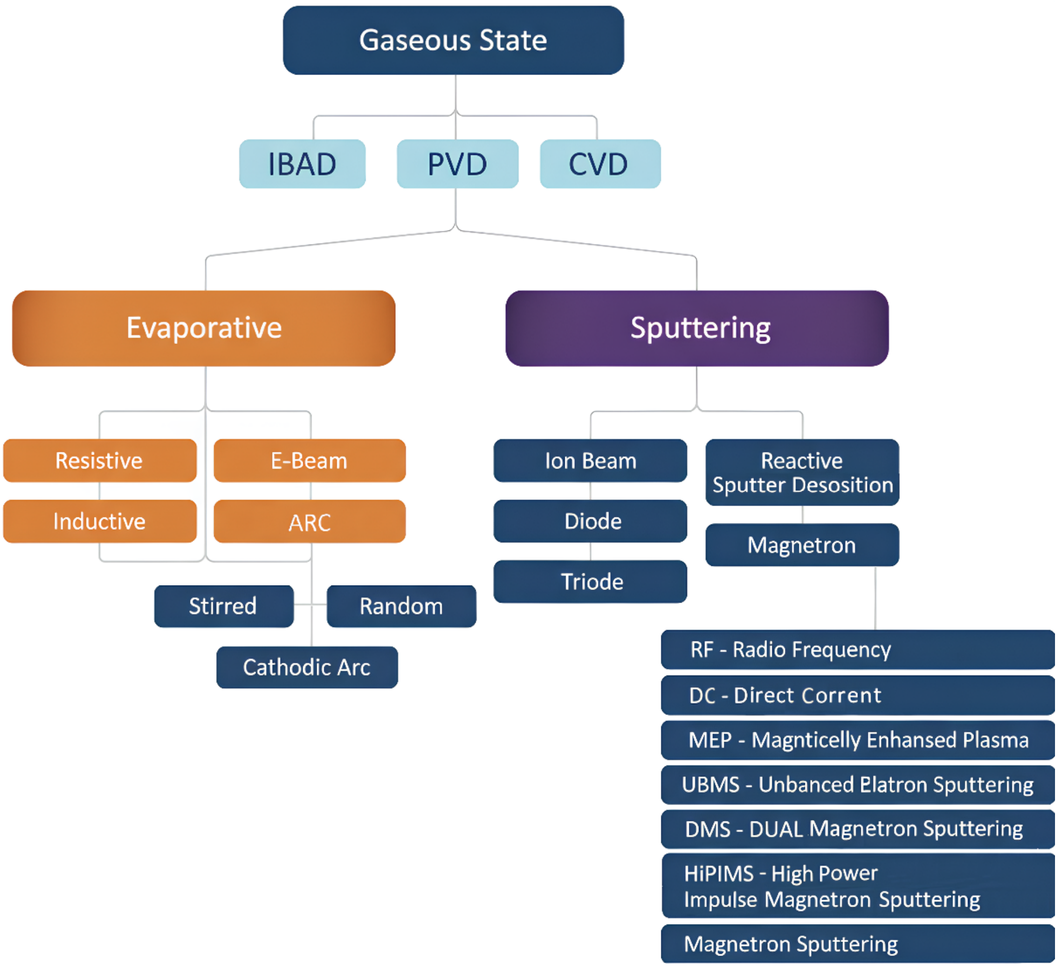


Figure 1. Surface coating methods.

In PVD techniques, carried out within a vacuum and under gaseous plasma conditions, the target material undergoes a physical–thermal process that transforms it into atomic particles. These particles are subsequently directed toward the substrate, where they condense or accumulate to form a physical coating. Figure 2 illustrates the sputtering deposition process, a PVD method. It details how ions from an inert gas bombard the target, releasing atoms that are deposited on the substrate to form the film.

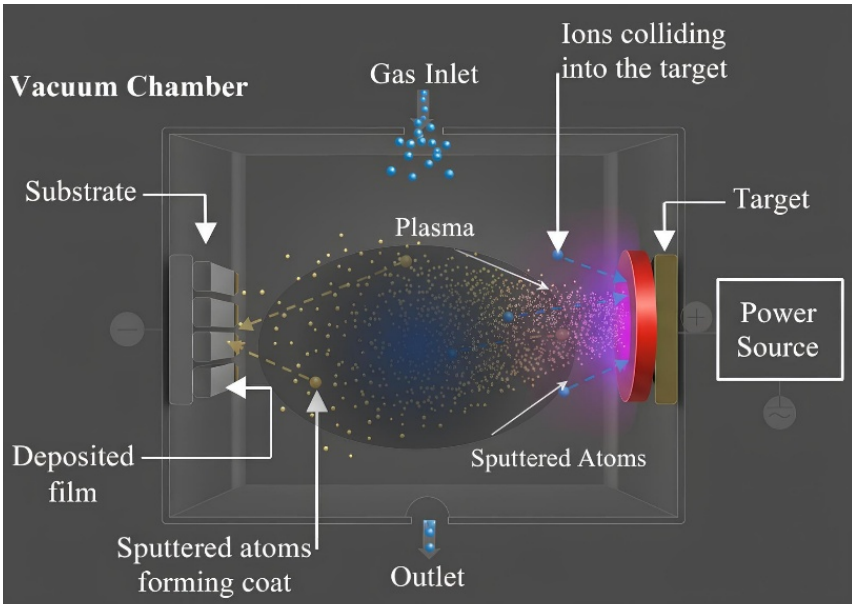


Figure 2. Schematic drawing of conventional PVD Sputtering process.

1.1.1. Evaporation Systems

The evaporation technique is a physical process in which the target, composed of the material to be deposited, acts as a cathode and serves as the evaporation source. This system can evaporate various materials depending on the power of the electron beam. Particles are released through electron bombardment in a vacuum environment. Gas molecules introduced into the reactor collide with the released particles, creating plasma. The resulting coating layers are deposited in a compressed manner, enhancing the film's adhesion to the substrate [50,62,63,65,66].

For instance, Arc Vapor Deposition [105] utilizes a high current, low voltage arc to vaporize either the anode electrode (anode arc) or the cathode electrode (cathode arc). The vaporized particles, being highly ionized, are deposited onto the substrate, which is positioned at an angle to optimize deposition and accelerate the process. In the Electron Beam (E-Beam) process, an electron gun is employed to vaporize the coating material, while a magnetic field directs the electrons from the gun to the target [106].

1.1.2. Sputtering Systems

The most widely used thin film deposition technique is PVD sputtering with DC magnetron [29]. In this process, the raw material, shaped as a target, is placed near a magnetron within a vacuum chamber. After depressurizing the chamber, an inert gas is introduced and accelerated by a high voltage applied between the target and substrate, directed towards the magnetron. This causes atomic sized particles to be ejected from the target, propelled by the kinetic energy transferred to the gas ions. These particles collide with the target and are projected onto the substrate, forming a solid thin film. This technique also allows for substrate cleaning, which eliminates localized contamination by reversing the voltage polarity between the target and substrate—a step known as cathodic cleaning [58].

To ensure proper film adhesion during the deposition process, substrate preparation is crucial. The first step involves cleaning the substrate, often performed in an ultrasonic bath outside the vacuum chamber [107]. If precleaning is not feasible, the sputtering vacuum chamber enables cleaning and subsequent coating deposition [58,107]. However, this cleaning phase is a disadvantage compared to other methods, as it is time-consuming, increasing the final product cost. Process times, along with setup times, significantly affect the overall cost. The cycle time must account for the vacuum chamber size and the capacity of the bombardment system [75].

Key parameters influence the success of the deposition process in terms of both cost and coating quality. For instance, the deposition rate is critical and depends on optimizing plasma density and the energy available during the process. Careful consideration of all essential parameters ensures the best combination to optimize the process for both quality and cost [108]. Once the setup is complete and the substrates are placed inside the vacuum chamber, the deposition process progresses through four stages, as illustrated in Figure 3.

The PVD sputtering process involves four key stages:

- Ramp up stage: During this stage, the chamber's temperature gradually increases while pressure decreases using a vacuum pump system. Typically, sputtering reactors employ two pumps: one for achieving primary vacuum (up to 10^{-5} bar) and another for high vacuum (up to 10^{-7} bar);
- Etching: This critical step ensures coating quality by enhancing film adhesion to the substrate. Plasma ions bombard the substrate, cleaning its surface of contaminants. Substrate properties, such as material composition, surface quality, and hardness, also play a significant role in adhesion [109,110];
- Coating thin films: The thin film forms as the deposited material accumulates on the substrate. Commonly used materials include titanium, zirconium, and chromium nitrides or oxides;

Ramp Down stage: This stage requires careful control to preserve coating quality. The chamber returns to ambient temperature and pressure, aided by a cooling system (chiller). While necessary, the cooling process increases energy consumption and reduces production rates.

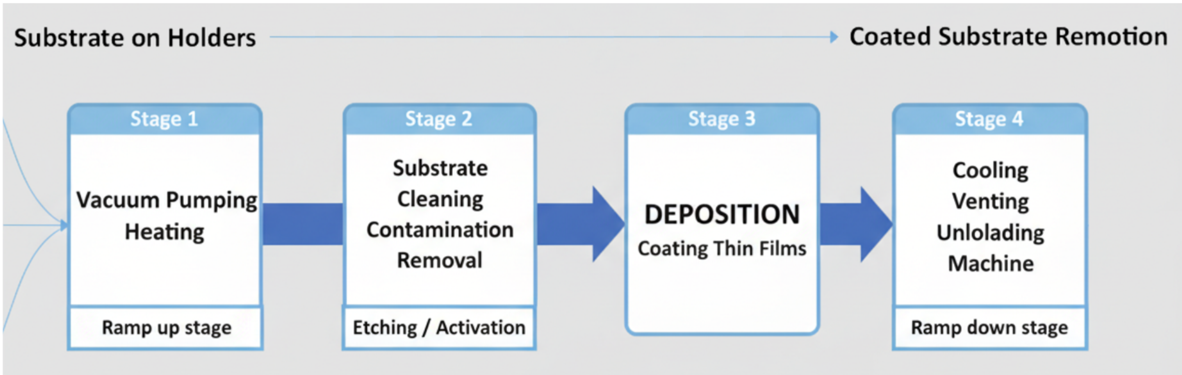


Figure 3. The processing flow for a classic PVD sputtering process.

There is a growing awareness of the need to protect the planet. Global concerns are focused on reducing energy consumption and production costs [111]. This shift is driving policies that encourage innovation in industrial processes. To enhance efficiency and optimize operations, new techniques and reactors have been developed, offering varied combinations and derivations.

One such advancement is High Power Impulse Magnetron Sputtering (HiPIMS) [112], a variation of PVD sputtering that employs short, high power current pulses to generate plasma. According to Gudmundsson [113], HiPIMS yields thin films with superior adhesion, higher density, and better overall quality compared to conventional DC or RF sputtering. Supporting this, Ghailane et al. [114] reviewed architectural design innovations in hard coatings achieved through HiPIMS, highlighting its potential in industrial applications.

Hybrid approaches also show promise. For instance, Geng et al. [115] combined magnetron sputtering with ion beam sputtering, producing films with high density and low roughness. Such hybrid methods underline the significance of optimizing key deposition parameters, including substrate polarization, frequency, global pressure, reactive gas partial pressure, duty cycle, gas type and volume, potential difference between the target and substrate, target power, temperature, and others.

Another noteworthy technology is Pulsed DC Magnetron Sputtering (PDMS), as explored by Greczynski et al. [116]. This variation of DC sputtering uses short, high power pulses to generate plasma, resulting in improved film quality, reduced arcing, and more efficient target utilization.

Recent studies further illuminate the impact of advanced techniques. Dong et al. [117] investigated the role of pulse frequency on film growth and properties. They found that increasing pulse frequency reduced deposition rates and transformed film microstructures from strongly columnar to column free and nearly fully dense. Additionally, film surfaces evolved from rough to smoother as frequency increased.

The review seeks to expand the academic understanding of TiAlN-based coatings for cutting tools by exploring the state of the art in doping elements, improvements in coating mechanical properties, and future challenges from an industrial perspective. It will also outline possible future studies to enrich research on this topic. TiAlN-based coatings will be organized into sections to ensure clarity and readability.

2. Coating Types—Architecture/Design

As previously discussed in this work, coatings can be designed with various architectures depending on their intended function. The microstructure and mechanical properties of these coatings are influenced by both their architectural design and chemical composition. Figure 4 illustrates several types of coatings applied to substrates, showcasing the following configurations: (a) Single layer coating; (b) Double layer coating; (c) Gradient coating; (d) Multilayer coating; (e) Nanolayer coating; and (f) Nanocomposite coating. Each type of coating architecture offers specific advantages and performance characteristics, tailored to meet the demands of different applications. For instance, single layer coatings might be suitable for simpler protective needs, while nanolayer and nanocomposite coatings offer advanced properties, such as higher hardness, reduced friction, and improved wear resistance. These variations underline the importance of selecting the appropriate coating architecture to optimize performance in accordance with the substrate's intended use.

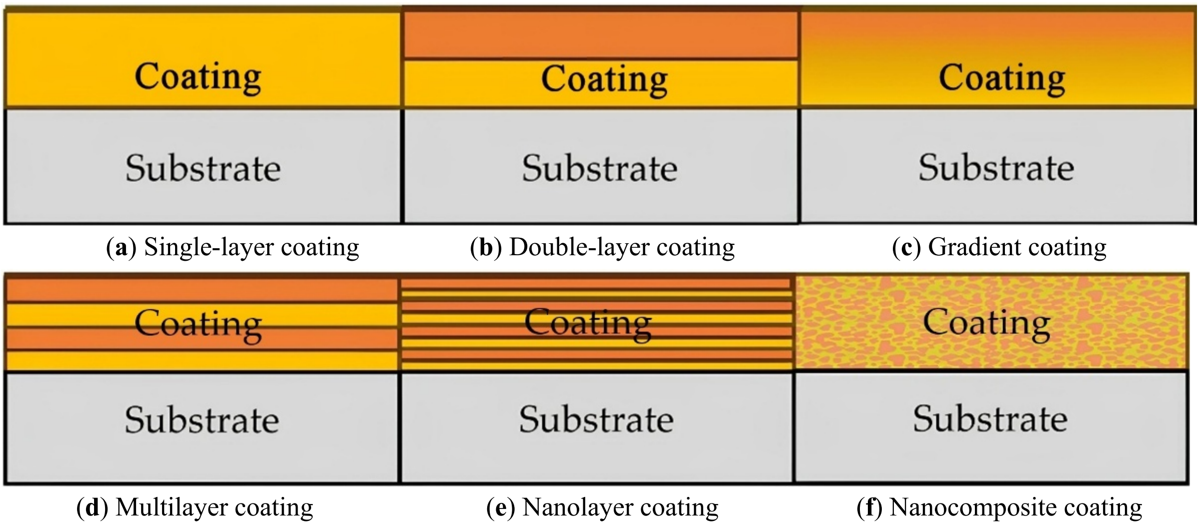


Figure 4. Different types of coating structure applied to substrates adapted by [1].

If the tool is expected to operate in an environment or under stress conditions that could lead to cracking, a Multilayer coating is recommended over a Single layer coating. This is due to the recognized advantage of Multilayer coatings in resisting crack propagation. Unlike Single layer coatings, Multilayer structures create barriers that slow or prevent the spread of cracks, enhancing the tool's durability and performance.

However, the number of layers in the coating must be carefully controlled to avoid negatively affecting other critical properties. For instance, the number of layers directly influences the hardness of the coating. It is, therefore, crucial to optimize this parameter to meet specific application requirements [62,65]. Figure 5 illustrates the typical patterns of crack propagation based on the coating structure, highlighting the superior resistance provided by Multilayer coatings compared to Single layer alternatives.

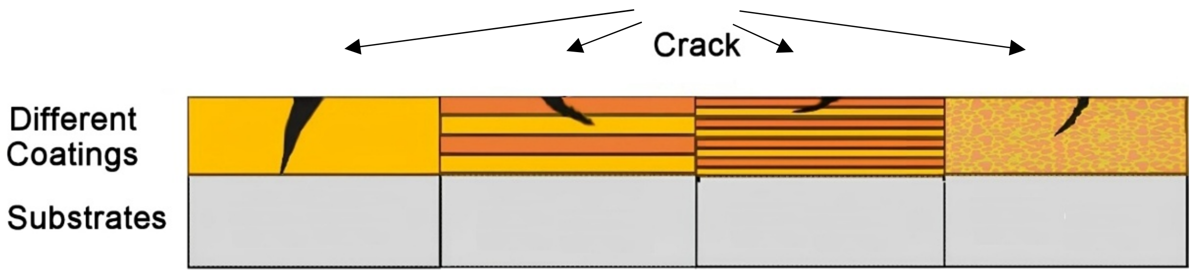


Figure 5. Common Crack propagation in coating structure adapted by [1].

When depositing the first layer of a coating, it is crucial to evaluate the need for an adhesion promoting layer, even if the elements used differ from those in the subsequent layers. Du et al. [104] investigated the impact of Cr and Ti interlayers on the structure of TiAlN-based coatings. In their study, four types of coatings with Cr and Ti interlayers on hard metal substrates were examined. The Cr interlayer displayed a mixed morphology of columnar and equiaxed crystals, while the Ti interlayer exhibited a predominantly columnar morphology. When comparing adhesion performance, the Cr interlayer demonstrated superior adhesion.

The elements incorporated into the coating layers impart diverse properties to the substrate, such as enhanced wear and corrosion resistance, improved thermal conductivity, and more. Studies by several authors [104,105,118–121] indicate that TiAlN coatings are well suited for high speed machining due to the formation of an oxide layer at the tool workpiece interface, which provides high oxidation resistance to the coating.

This work aims to present the state of the art and the evolution of TiAlN-based coatings, assessing the intrinsic properties of various coatings. A comprehensive review of studies by other researchers will highlight applications in the industrial context, particularly in machining processes like turning and milling. The focus will be on the properties acquired through TiAlN-based coatings and their progression when doped with additional elements. Detailed analyses will be provided on their structure, micro structure, chemical composition, and the influence on mechanical properties such as hardness and Young's modulus (elasticity).

Furthermore, studies examining the performance of these coatings, the mechanisms of wear, and their impact on energy consumption in machining will be analyzed. This will help identify pathways to enhance machining efficiency and extend tool lifespan [121].

3. Influence of the Dopant Elements in TiAlN-Based Regarding the Coating Types Architecture

Since its development in 1970, TiAlN coating has proven to be an effective solution for enhancing tool performance and durability, especially in high speed machining applications. Renowned for their beneficial properties and reliability, TiAlN and its derivatives remain a focal point of interest for both industry and the scientific community. Recent advancements, highlighted in contemporary studies, show that the introduction of novel doping elements has further enhanced the performance of TiAlN-based coatings.

Compared to multilayer architectures, single-layer coatings have more homogeneous microstructures and easier-to-control residual stresses, offering good thermal stability and competitive performance in specific applications. However, multilayer systems benefit from greater resistance to crack propagation due to internal interfaces, as well as improved properties such as hardness and adhesion to the substrate.

This section explores these developments by presenting studies that investigate the effects of various dopants, including Silicon (Si), Tantalum (Ta), Yttrium (Y), Chromium (Cr), Molybdenum (Mo), Vanadium (Va), and Ruthenium (Ru). The discussion is structured according to the coating architectures depicted in Figure 5, with particular attention to the resulting mechanical properties, such as hardness, Young's modulus, wear resistance, and their implications for tool lifespan. The analysis begins with coatings featuring Single layer structures, progresses to Multilayer designs, and concludes with nanolayer configurations.

3.1. Single Layer Coating

Yang et al. [122] presented, in their study of TiAlN-based films, the influence of the addition of the Mo element. In the work, the authors varied the amounts of Mo. In this study, the mechanical properties of each set of samples were analyzed, as well as the microstructure of the TiAlMoN films. The authors stated that hardness and Young's Modulus increased with increasing Mo addition. The maximum hardness value achieved for the 12.1% Mo content was 50 GPa and the Young's Modulus value was 610 GPa. The authors also studied microstructure obtained using SEM images of the coating's cross section and concluded that the structure of the film with a content of 2.8 at.% presents some non-uniform columnar grains. For a content of 12.1 at.% a columnar structure is observed. They also concluded that the wear behavior of TiAlMoN films did not increase with the Mo content according to the analysis of wear performance through the H/E ratio (hardness/Young's Modulus). Tomaszewski et al. [123] also study the influence of the addition of the Mo element. The results showed that the coating with 7.7 at.% Mo, had significant improvement in the coating wear behavior, as well as corrosion resistance.

Yi et al. [124] studied the influence of adding the element Ni to TiAlN-based coatings because, according to the authors, the addition of Ni influences the microstructure, like Mo. In their study, three sets of AlTiN-Ni samples with different Ni contents were used. Subsequently, these samples were tested in the turning process with the Inconel 718 material. The contents studied were 0%, 1.5%, and 3% Ni. In this study, the deposition process was PVD cathodic arc evaporation. The structure obtained was columnar with clear evidence of the importance of Ni in promoting the homogenization of the structure, nanocrystalline. The hardness and Young's modulus values obtained showed that they decreased with increasing Ni content. The authors also observed that the toughness of the coating with the 1.5 at.% Ni was the highest, having a 160% increase in tool life.

Liu et al. [125] studied the influence of adding the element Ruthenium (Ru) with different Ruthenium contents: 0%, 7% and 15% in TiAlN-based coatings. Like the study done by Yi et al. [124], the influence of the addition of the Ru element promoted homogenization of the microstructure. With increasing Ru content, the structure changed from columnar to a homogeneous structure. The mechanical properties were also studied and, according to the authors, for a content of 7% Ru the hardness and Young's Modulus were 33.15 GPa and 498.55 GPa respectively. Therefore, there was an increase. However, for a 15% Ru content, the hardness and Young's Modulus decreased slightly even when compared to the TiAlN base coating.

Aninat et al. [126] studied the effects caused by the addition of the elements Tantalum (Ta) and Yttrium (Y) to TiAlN-based coatings. Coating with the addition of Y showed an increase in hardness values. Ta did not have a significant influence on the mechanical properties, only having an influence on the amount of residual compressive stresses. These stresses are linked to the wear behavior of the coating. In summary, the authors concluded that Ta-doped coatings obtained better wear behavior, while Y-doped coatings obtained better mechanical properties. Chandra et al. [127] studied the influence of the thickness of the TiAlN coating. They concluded that the mechanical properties changed little with the variation in thickness, with an insignificant decrease with the increase in thickness. However, regarding residual stresses, these are greatly influenced by the thickness of the coating. For example, residual stress increases with decreasing thickness. Therefore, the authors state that there are greater stresses for thinner coatings.

Das, S. et al. [128] studied another element, Silicon (Si), in this work, the authors concluded that the Si doping element in the TiAlN coating causes a significant increase in mechanical properties, such as hardness and Young's Modulus. They also found an improvement in wear behavior when compared to the TiAlN coating. In this scientific work, two TiAlN coatings with a high aluminum content, with different structures, were studied. One of the coatings had a fine-grained structure, with cubic and hexagonal faces, the other had a coarse-grained structure with cubic faces. Despite the films having a similar chemical composition, the difference in structure caused a different reaction regarding thermal behavior, with emphasis on controlling the coating structure to obtain the desired result, regarding thermal stability.

3.2. Multilayer Coating

In industry, where machining is predominant, tools with multilayer coating are widely used. These coatings allow you to combine different properties to optimize the process, improve machining quality and increase tool life. Another advantage is associated with the growth of cracks with its multilayer structure, with this type of structure the growth of cracks is very reduced [65]. This characteristic becomes very attractive for industry, particularly for the milling and turning sector [129].

In a recent study, Zhang et al. [130] improved the TiAlN-based multilayer coating by making combinations of Ti/TiAlN, TiAlN/TiN, and TiN/TiAlN for coating thicknesses of 0.15 and 0.3 µm. In this study, the authors studied cyclic oxidation and in relation to the results, it was noted that the coating with the thicker Ti layer had an increase in compressive residual stress and did not present cracks due to the thicker ductile Ti layers. Çomakli [131] carried out a study, comparing the mechanical and corrosion properties of tools coated with TiN, TiAlN and TiAlN/TiN multilayers. According to the authors, they concluded that the multilayer coating presented a smoother surface, with a smaller grain, compared to the other coatings studied. The hardness increased due to the number of layers, in line with what has been documented in works by other authors [65,129]. In this work, the authors also concluded that the friction coefficient decreased, leading to a lower wear rate. This conclusion is in line with the results of another study previously carried out by Çomakli, where the use of chromium nitride (CrN) is studied. In this study, the author compares the mechanical properties and wear performance with the TiAlN monolayer coating and concludes that reducing the friction coefficient improves the wear behavior and coating properties.

Liu et al. [132], studied multilayer coatings to mitigate some problems associated with significant energy losses and machine failures due to friction and wear of some components. The use of multilayer coatings can combine different dopings with different physical and chemical properties in order to improve some coating properties. Their work reviews multilayer coatings, including transition metal nitride coatings, diamond like carbon-based coatings, and other multilayer coatings. The authors concluded that there are still many problems to be resolved and this is a valid reason for research in this area to evolve. They also found that coatings with multilayer structures have a much lower Coefficient of Friction (COF) when compared to multilayer coatings with different structures or single layer coatings.

Zhang et al. [133] concluded in their study that the addition of Ti intermediate layers improved the wear performance of the multilayer coating. Shugurov et al. [134] when studying the influence of TiAl interlayers on a TiAlN-based multilayer coating and the most appropriate thickness, they concluded that the most favorable results were three TiAl interlayers and four TiAlN layers, with thicknesses of 0.2 and 0.6 µm respectively. This work is a reference for other research work because the method used can be used in a wide range of applications, particularly in machining. The use of Ta as doping in the TiAlN-based coating with multilayers and different thicknesses was the focus of study by some Silva et al. [135]. Shang et al. [136] studied the properties obtained with the thin film with TiAlN/Ta multilayers being distributed as follows: (a) one layer of TiAl; (b) another of TiAlN and the last of Ta. In this work, the results were compared with monolithic TiAlN coatings, concluding that the coating under study had higher hardness and Young's modulus, 31 GPa and 315 GPa respectively, corresponding to an increase of 29% and 47% respectively. According to the literature, the element, Ta, is a ductile material and due to this characteristic, it can dissipate energy through deformation, making the propagation of cracks difficult. This element also provides better thermal stability. These last two studies [135,136] show that the element, Ta, improves the wear behavior of the TiAlN-based coating, meeting the recognized characteristic of Ta, ductility. The results obtained with the coating can be replicated with other substrates, with different properties, according to the study by Zhao et al. [137]. In this study, coatings were tested with 2, 5, 7 and 10 alternating layers of TiAlSiN whose deposition process varied the chamber pressures to obtain different hardnesses, 0.08 and 0.2Pa. The authors highlighted in the results the hardness and Young's modulus with the highest value was obtained with the highest chamber pressure, 0.2 Pa. However, the best result regarding resistance to plastic deformation and consequently the lowest wear rate was obtained in the coating with 5 layers. Coatings with 5 or more layers had similar wear rates.

Baptista et al. [138] compared the performance of TiAlSiN coatings, deposited by HiPIMS, on tools used for milling Duplex Stainless Steel (DSS). The work focused on structural distinction, comparing a single layer configuration with an optimized multilayer structure. Machining results showed that the multilayer structure exhibited better performance, consistently demonstrating better surface quality and less sustained wear (flank and overall), especially under longer cutting length conditions (10 m). At the mechanical level, the multilayer structure promoted greater hardness and greater adhesion resistance, resulting in smoother wear mechanisms (predominance of light adhesion and abrasion). The authors concluded that the multilayer architecture is fundamental to maximizing wear resistance and tool lifespan when machining DSS.

The scientific community has also shown interest in multilayer nano coatings due to the ability to obtain very thin layers. Next, the work that has been done regarding nanolayer coatings will be explored.

3.3. Nanolayer Coating

One of the characteristics associated with nanolayer coatings is their ability to resist crack propagation. Due to the greater number of layers, these coatings have greater resistance to crack propagation, and normally also have higher hardness values. The most recent studies focused on new monolayer coatings based on TiAlN, together with doping elements such as Mo, Ta, Y and Cr, show a significant improvement in mechanical properties. Next, some work will be presented involving the application of machining, turning and milling, with coated tools, emphasizing the types of wear that the tools are subject to. For example, Bonu et al. [139] did a study comparing Ti/TiN and TiAl/TiAlN, nanometer scale, ultrathin multilayer coatings. These coatings provided better mechanical resistance, higher hardness, better adhesion and better anticorrosion performance. The erosion resistance of the studied coatings was significantly higher when compared to the studied substrate, Ti6Al4V. Corrosion resistance improved by approximately 3.5% when compared to the Ti6Al4V substrate in NaCl solution. In nanolayer coatings the height of the layers is smaller compared to normal multilayer coatings. For this reason, for a coating with the same thickness, the nanolayer coating has a greater number of layers. This fact helps to improve the hardness, as well as the resistance to crack propagation of the coating. Wang et al. [140] studied the influence of layer thickness on TiN/TiAlN nanolayer coatings, carrying out the characterization, observing the mechanical properties and wear behavior. In this work, the authors were able to define the size of the layer thickness by controlling the rotational speed of the coating deposition. The authors determined the thickness in order to obtain the best mechanical properties, such as hardness and Young's modulus. Like the characteristic of the nanolayer coating, it also improved resistance to crack propagation.

Table 1, presents a studies summary that investigates the effects of various dopants, including Silicon (Si), Tantalum (Ta), Yttrium (Y), Chromium (Cr), Molybdenum (Mo), Vanadium (Va), and Ruthenium (Ru), for different coating types.

Following a SWOT analysis of the studies mentioned in the previous table, which relates the type of coating to the addition of doping elements, the strengths, weaknesses, opportunities and threats are presented.

The identified forces are:

- The introduction of doping elements in the thin film deposition process improves the characteristics and properties of coatings. For example: (a) Wear Resistance: Ta, Cr, and V help increase wear resistance; (b) Corrosion Resistance: Ta, Cr, Y, Ru, and Si increase the coating's resistance to oxidation and corrosion in aggressive environments; (c) High Temperature Stability: Ta, Y, Si, and Cr improve the coating's high temperature performance, providing thermal stability; (d) Mechanical Properties: Cr, V, Ru, Si, Mo, and Y increase hardness and strength; (e) Adhesion: Y helps improve adhesion and grain structure.

- Coefficient of Friction (COF): Reduced with multilayer coatings (TiAlN, TiSiN).
- Crack Propagation: Reduced with multilayer coatings, nanolayers, and nanocomposites.

Table 1. Main results for different types of TiAlN-based coatings.

Coating Type	Study/Authors	Dopants/Interlayer Material	Key Results & Performance Impact
Single layer coating	Yang et al. [122]	Mo (Molybdenum)	Increased hardness (max. 50 GPa) and Young's Modulus (max. 610 GPa) with 12.1% Mo. Structure altered to uniform columnar. Wear behavior did not improve proportionally with Mo content.
	Tomaszewski et al. [123]	Mo (Molybdenum)	Maximum improvement in wear and corrosion resistance with 7.7% Mo.
	Yi, J. et al. [124]	Ni (Nickel)	Better structural homogenization with 1.5% Ni, 160% increase in tool life. Hardness and Young's Modulus decreased with higher Ni content.
	Liu et al. [125]	Ru (Ruthenium)	Structural homogenization increased with Ru. Hardness and Young's Modulus increased with 7% Ru but decreased at 15%.
	Aninat et al. [126]	Ta (Tantalum) and Y (Yttrium)	Ta improved wear behavior; Y increased mechanical properties such as hardness.
	Chandra et al. [127]	Coating thickness	Residual stresses increased with thinner coatings, affecting wear behavior.
	Das, S. et al. [128]	Si (Silicon)	Significant increase in hardness and thermal stability; improved wear behavior.
Multilayer coating	Zhang et al. [130]	Ti/TiAlN, TiAlN/TiN, TiN/TiAlN	Thicker Ti layers increased compressive stress and improved cutting performance.
	Çomakli [131]	TiN, TiAlN, TiAlN/TiN	Multilayer coatings showed lower friction coefficient and wear rate, with increased hardness due to layer number.
	Liu et al. [132]	Multilayers with different materials	Multilayer coatings had significantly lower Coefficient of Friction (COF).
	Shugurov et al. [134]	TiAl interlayers	Best performance with 3 TiAl and 4 TiAlN layers.
	Silva et al. [135]	TiAlTaN	The study focuses on TiAlN-based coating with Multilayers and different thicknesses.
	Shang et al. [136];	Ta (Tantalum)	29% increase in hardness and 47% in Young's Modulus. Improved thermal and wear behavior due to Ta ductility.
	Zhao et al. [137]	TiAlSiN	5 layer coatings showed the lowest wear rate. Best performance obtained at 0.2 Pa chamber pressure.
Nanolayer coating	Bonu et al. [139]	Ti/TiN and TiAl/TiAlN	Improved mechanical and anticorrosion resistance compared to Ti6Al4V. Nanolayers increased hardness and crack propagation resistance.
	Wang et al. [140]	TiN/TiAlN	Layer thickness directly influenced mechanical properties. Optimal thickness determined for maximum hardness and Young's Modulus.

Weaknesses include:

- Complex processes that are sensitive to deposition parameters, as well as the technology used.
- High cost and difficult control of thin layers.
- Residual stresses introduced during the deposition process can reduce adhesion—Lack of homogeneity between very thin layers.
- Performance is not always proportional to doping.

Opportunities include:

- Applications in high performance sectors such as aerospace and automotive.
- Integration with simulations and computational optimization.
- Development of new multicomponent systems.
- Advances in nanotechnology and surface engineering. Multilayer systems with different doping elements to improve coating performance.

Threats include:

- Competition from alternative technologies, such as CVD, which also offer good results.
- Thermal failures limit industrial use.
- Dependence on critical and expensive materials (such as the doping elements chromium (Cr), vanadium (V), ruthenium (Ru), silicon (Si), molybdenum (Mo), tantalum (Ta) and yttrium (Y), among others).
- Lack of process standardization.
- Difficulties in finetuning the deposition process parameters to optimize it.
- Excessive complexity without proportional gains.

4. Concluding Remarks

The importance of hardfacing cutting tools for preserving edge integrity, reducing friction and lowering temperatures during the machining process is widely recognised, and several studies on TiAlN-based coatings have already been conducted. However, the scientific community still lacks a clear understanding of the correlation between the various parameters that influence their efficiency.

After analyzing the values obtained in reviewed works, in general, the introduction of elements in the coating process brought significant improvements. The most relevant were the following: In corrosion resistance, the improvement ranged between 10–15%, hardness was between 25–30%, and Young's modulus was 40–50%, thermal resistance 15–20%, coefficient of friction was between 20–30%, improving the tool lifespan above 130–150%.

Therefore, it is necessary to continue studies and testing on coatings for cutting tools, for instance:

- adding the dopant element according to the desired properties to achieve a good functional response and thus extend tool lifespan. Also, combining different types of coating structure applied to substrates with a single dopant or different dopants; and
- testing different deposition technologies for the same type of coating, such as PVD sputtering and HiPIMS. Comparative studies between these two technologies should include the cost per tool, taking into account the deposition process, tool lifespan and machining quality achieved.
- a detailed analysis of TiAlN-based coatings confirms that optimising properties such as wear resistance (via dopants such as Ta, Cr and V) and thermal stability (via Ta, Y and Si) is dependent on modifying the elements and microstructure. However, future research should consider more than just the optimisation of individual properties.
- a detailed lifespan analysis should be conducted to compare established TiAlN systems (and their doped variations) with emerging AlCrN or AlTiCrN systems, in order to determine their long-term sustainability, economic viability and technical performance.
- furthermore, it would be important to investigate the impact of using multiple dopants rather than a single dopant on reducing the coefficient of friction (COF) in multilayer systems at high temperatures. This would help to simulate more rigorous industrial operating conditions and identify compositions that maximise energy efficiency.
- The most promising technological frontier lies in the integration of Artificial Intelligence (AI)-based deposition control for predictive optimisation, which is essential for overcoming the limitations of the trial-and-error method. This is done by correlating process parameters with the final properties of the coating in real time.

Future research should focus on bridging the gap between laboratory-scale deposition and industrial-scale deposition. It is also important to validate optimal doping and process parameters in high-volume production environments.

Author Contributions

G.F.P.: conceptualization; G.F.P. and F.J.G.S.: methodology; G.F.P.: writing—original draft preparation; A.B., G.F.P., N.P.V.S. and F.F.: investigation; F.J.G.S.: supervision; E.S. and R.A. validation; F.J.G.S., A.B., F.F.: writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

Funding

The work is developed under the "DRIVOLUTION-Transition to the factory of the future", with the reference DRIVOLUTION C644913740-00000022 research project, supported by European Structural and Investments Funds with the "Portugal2020" program scope.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Not applicable.

Conflicts of Interest

Given the role as Editor-in-Chief, Francisco J. G. Silva had no involvement in the peer review of this paper and had no access to information regarding its peer-review process. Full responsibility for the editorial process of this paper was delegated to another editor of the journal. The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

References

1. Sousa, V.F.C.; Silva, F.J.G.; Pinto, G.F.; et al. Characteristics and Wear Mechanisms of TiAlN-Based Coatings for Machining Applications: A Comprehensive Review. *Metals* **2021**, *11*, 260.
2. Kulkarni, B.H.; Nadakatti, M.M.; Kulkarni, S.C.; et al. Investigations on effect of nanofluid based minimum quantity lubrication technique for surface milling of Al7075-T6 aerospace alloy. *Mater. Today Proc.* **2020**, *27*, 251–256.
3. Mersni, W.; Boujelbene, M.; Salem, S.B.; et al. Machining time and quadratic mean roughness optimization. *Mater. Today Proc.* **2020**, *26*, 2619–2624.
4. Gabiccini, M.; Bracci, A.; Battaglia, E. On the estimation of continuous mappings from cradle-style to 6-axis machines for face-milled hypoid gear generation. *Mech. Mach. Theory* **2011**, *46*, 1492–1506.
5. Moriya, T.; Nakamoto, K.; Ishida, T.; et al. Creation of V-shaped microgrooves with flat-ends by 6-axis control ultraprecision machining. *CIRP Ann.* **2010**, *59*, 61–66.
6. Özlü, B.; Ulaş, H.B.; Kara, F. Investigation of the Effects of Cutting Tool Coatings and Machining Conditions on Cutting Force, Specific Energy Consumption, Surface Roughness, Cutting Temperature, and Tool Wear in the Milling of Ti6Al4V Alloy. *Lubricants* **2025**, *13*, 363.
7. Sharma, N.; Chawla, V.; Ram, N. Computer numerical control machine. *Int. J. Data Network Sci.* **2020**, *4*, 1–14.
8. Wu, Y.; Yue, N.; Qien, K. Performance optimization of CNC machine tool system based on sensor data. *Sci. Program.* **2022**, *2022*, 5663824.
9. Siddiqui, T.U.; Singh, S.K. Design, fabrication and characterization of a self-lubricated textured tool in dry machining. *Mater. Today Proc.* **2020**, *41*, 863–869.
10. Dittrich, M.A.; Uhlich, F.; Denkena, B. Self-optimizing tool path generation for 5-axis machining processes. *CIRP J. Manuf. Sci. Technol.* **2019**, *24*, 49–54.
11. Pimenov, D.Y.; Bustillo, A.; Wojciechowski, S.; et al. Artificial intelligence systems for tool condition monitoring in machining: Analysis and critical review. *J. Intell. Manuf.* **2022**, *34*, 2079–2121.
12. Serin, G.; Sener, B.; Ozbayoglu, A.M.; et al. Review of tool condition monitoring in machining and opportunities for deep learning. *Int. J. Adv. Manuf. Technol.* **2020**, *109*, 953–974.
13. Zhang, X.; Han, C.; Luo, M.; et al. Tool wear monitoring for complex part milling based on deep learning. *Appl. Sci.* **2020**, *10*, 6916.
14. Proteau, A.; Tahan, A.; Thomas, M. Specific cutting energy: A physical measurement for representing tool wear. *Int. J. Adv. Manuf. Technol.* **2019**, *103*, 101–110.
15. Ravikumar, S.; Ramachandran, K. Tool wear monitoring of multipoint cutting tool using sound signal features signals with machine learning techniques. *Mater. Today Proc.* **2018**, *5*, 25720–25729.
16. Saw, L.H.; Ho, L.W.; Yew, M.C.; et al. Sensitivity analysis of drill wear and optimization using adaptive neuro fuzzy-genetic algorithm technique toward sustainable machining. *J. Clean. Prod.* **2018**, *172*, 3289–3298.
17. Kothuru, A.; Nooka, S.P.; Liu, R. Application of audible sound signals for tool wear monitoring using machine learning techniques in end milling. *Int. J. Adv. Manuf. Technol.* **2018**, *95*, 3797–3808.

18. Ferrando Chacón, J.L.; Fernández de Barrena, T.; García, A.; et al. A novel machine learning-based methodology for tool wear prediction using acoustic emission signals. *Sensors* **2021**, *21*, 5984.
19. Pinto, G. Experimental Study on PVD DC Sputtering Thin Films: Efficiency, Coating Properties, And Wear Tools Performance on Milling Pre-Hardness Tools Steels. Ph.D. Thesis, University of Vigo, Vigo, Spain, 2024.
20. Kamar, M.T.; Elattar, H.; Mahmoud, A.S.; et al. A Critical Review of State-of-the-Art Technologies for Electroplating Wastewater Treatment. *Int. J. Environ. Anal. Chem.* **2022**, *104*, 4143–4176. https://doi.org/10.1080/03067319.2022.2098486.
21. Kumar, V.; Dwivedi, S.K. Toxicity Potential of Electroplating Wastewater and Its Bioremediation Approaches: A Review. *Environ. Technol. Rev.* **2021**, *10*, 238–254.
22. Comparini, A.; Del Pace, I.; Giurlani, W.; et al. Electroplating on Al6082 Aluminium: A New Green and Sustainable Approach. *Coatings* **2022**, *13*, 13.
23. Passaponti, M.; Lari, L.; Bonechi, M.; et al. Optimisation Study of Co Deposition on Chars from MAP of Waste Tyres as Green Electrodes in ORR for Alkaline Fuel Cells. *Energies* **2020**, *13*, 5646.
24. Mariani, E.; Giurlani, W.; Bonechi, M.; et al. A Systematic Study of Pulse and Pulse Reverse Plating on Acid Copper Bath for Decorative and Functional Applications. *Sci. Rep.* **2022**, *12*, 18175.
25. Giurlani, W.; Dell'Aquila, V.; Vizza, M.; et al. Electrodeposition of Nanoparticles and Continuous Film of CdSe on N-Si (100). *Nanomaterials* **2019**, *9*, 1504.
26. Giurlani, W.; Fidi, A.; Anselmi, E.; et al. Specific Ion Effects on Copper Electroplating. *Colloids Surf. B Biointerfaces* **2023**, *225*, 113287.
27. Martinuzzi, S.M.; Donati, L.; Giurlani, W.; et al. A Comparative Research on Corrosion Behavior of Electroplated and Magnetron Sputtered Chromium Coatings. *Coatings* **2022**, *12*, 257.
28. Kelly, P.J.; Arnell, R.D. Magnetron Sputtering: A Review of Recent Developments and Applications. *Vacuum* **2000**, *56*, 159–172.
29. Baptista, A.; Silva, F.; Porteiro, J.; et al. Sputtering Physical Vapour Deposition (PVD) Coatings: A Critical Review on Process Improvement and Market Trend Demands. *Coatings* **2018**, *8*, 402.
30. Baptista, A. Efficiency, coating properties, and machining performance of thin films deposited using HiPIMS: An experimental analysis. Ph.D. Thesis, University of Vigo, Vigo, Spain, 2024.
31. Faraday, M.X. The Bakerian Lecture. Experimental Relations of Gold (and Other Metals) to Light. *Philos. Trans. R. Soc. Lond.* **1857**, *147*, 145–181.
32. Nahrwold, R. The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light. *Ann. Physik* **1887**, *31*, 467.
33. Holland, L. *Vacuum Deposition of Thin Films*; Chapman & Hall: London, UK, 1958. ISBN 9780412053801.
34. Vorobyova, M.; Biffoli, F.; Giurlani, W.; et al. PVD for decorative applications: A review. *Materials* **2023**, *16*, 4919.
35. Berghaus, B. Improvements in and Related to the Coating of Articles by Means of Thermally Vapourized Material. UK Patent 510992, 1938.
36. Powell, C.F.; Oxley, J.H.; Blocher, J.M. *Vapour Deposition*; John Wiley & Sons: New York, NY, USA, 1966.
37. Jawaid, A.; Koksal, S.; Sharif, S. Cutting Performance and Wear Characteristics of PVD Coated and Uncoated Carbide Tools in Face Milling Inconel 718 Aerospace Alloy. *J. Mater. Process. Technol.* **2001**, *116*, 2–9.
38. Ichou, H.; Arrousse, N.; Berdimurodov, E.; et al. Exploring the Advancements in Physical Vapor Deposition Coating: A Review. *J. Bio Tribo Corros.* **2024**, *10*, 3.
39. Rossnagel, S.M. Sputter Deposition for Semiconductor Manufacturing. *IBM J. Res. Dev.* **1999**, *43*, 163–179.
40. Baptista, A.; Pinto, G.; Silva, F.J.G.; et al. Wear Characterization of Chromium PVD Coatings on Polymeric Substrate for Automotive Optical Components. *Coatings* **2021**, *11*, 555.
41. Bandinelli, R.; Fani, V.; Bindi, B. Electroplating and PVD Finishing Technologies in the Fashion Industry: Perspectives and Scenarios. *Sustainability* **2021**, *13*, 4453.
42. New York University; Office of Special Services for Business and Industry; American Vacuum Society; Vacuum Metallurgy Division. *Transactions of the Vacuum Metallurgy Conference*, 8th ed.; New York University Press: New York, NY, USA, 1966.
43. Bunshah, R.F. *New Trends in Materials Processing*; American Society for Metals: Metals Park, OH, USA, 1976.
44. Paton, B.A.; Movchan, B.A.; Demchishin, A.V. Structure and Properties of Electron-Beam Evaporated Massive Vacuum Deposits. In Proceedings of the 4th International Conference on Vacuum Metallurgy, Tokyo, Japan, 4–8 June 1973; p. 251.
45. Mattox, D.M.; McDonald, J.E. Interface Formation during Thin Film Deposition. *J. Appl. Phys.* **1963**, *34*, 2493–2494.
46. Mattox, D.M. *Handbook of Physical Vapor Deposition (PVD) Processing Film Formation, Adhesion, Surface Preparation and Contamination Control*; Knovel: Norwich, NY, USA, 1998.
47. Rubshtein, A.P.; Vladimirov, A.B.; Korkh, Y.V.; et al. The composition, structure and surface properties of the titanium-carbon coatings prepared by PVD technique. *Surf. Coat. Technol.* **2017**, *309*, 680–686.
48. Silva, F.J.G.; Martinho, R.P.; Alexandre, R.; et al. Wear resistance of TiAlSiN thin coatings. *J. Nanosci. Nanotechnol.* **2012**, *12*, 9094–9101.

49. Sam, Z. *Thin Films and Coatings: Toughening and Toughness Characterization*, 1st ed.; CRC Press: Boca Raton, FL, USA, 2015; pp. 377–463.
50. Silva, F.J.G.; Neto, M.A.; Fernandes, A.J.S.; et al. Adhesion and wear behaviour of NCD coatings on Si3N4 by micro-abrasion tests. *J. Nanosci. Nanotechnol.* **2009**, *9*, 3938–3943.
51. Martinho, R.P.; Silva, F.J.G.; Alexandre, R.J.D.; et al. TiB_2 Nanostructured coating for GFRP injection moulds. *J. Nanosci. Nanotechnol.* **2011**, *11*, 5374–5382.
52. Musil, J. Flexible hard nanocomposite coatings. *RSC Adv.* **2015**, *5*, 60482–60495.
53. Yang, Q.; Zhao, L.R. Microstructure, mechanical and tribological properties of novel multi-component nanolayered nitride coatings. *Surf. Coat. Technol.* **2005**, *200*, 1709–1713.
54. Veprek, S.; Veprek-Heijman, M.G.J.; Karvankova, P.; et al. Different approaches to super hard coatings and nanocomposites. *Thin Solid Films* **2005**, *476*, 1–29.
55. Silva, F.J.G.; Martinho, R.P.; Baptista, A.P.M. Characterization of laboratory and industrial CrN/CrCN/diamond-like carbon coatings. *Thin Solid Films* **2014**, *550*, 278–284.
56. Martinho, R.P.; Andrade, M.F.C.; Silva, F.J.G.; et al. Microabrasion wear behaviour of TiAlCrSiN nanostructured coatings. *Wear* **2009**, *267*, 1160–1165.
57. Mubarak, A.M.A.; Hamzah, E.H.E.; Tofr, M.T.M. Review of Physical Vapour Deposition (PVD) Techniques for Hard Coating. *Jurnal Mekanikal* **2005**, *20*, 42–51.
58. Mattox, D.M. *The Foundations of Vacuum Coating Technology*; Noyes Publications: Norwich, UK, 2003.
59. Martin, P.M. *Handbook of Deposition Technologies for Films and Coatings*, 3rd ed.; Elsevier: Amsterdam, The Netherlands, 2010.
60. Holmberg, K.; Matthews, A. *Coatings Tribology: Properties, Mechanisms, Techniques and Applications in Surface Engineering*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2009; p. 576.
61. Tracton, A.A. *Coatings Technology Handbook*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2006.
62. Tracton, A.A. *Coatings Technology: Fundamentals, Testing, and Processing Techniques*; CRC Press: Boca Raton, FL, USA, 2007; pp. 238–284.
63. Baptista, A.; Silva, F.J.G.; Porteiro, J.; et al. On the Physical Vapour Deposition (PVD): Evolution of Magnetron Sputtering Processes for Industrial Applications. *Procedia Manuf.* **2018**, *17*, 746–757.
64. Michailidis, N. Variations in the cutting performance of PVD-coated tools in milling Ti6Al4V, explained through temperature-dependent coating properties. *Surf. Coat. Technol.* **2016**, *304*, 325–329.
65. Inspektor, A.; Salvador, P.A. Architecture of PVD coatings for metalcutting applications: A review. *Surf. Coat. Technol.* **2014**, *257*, 138–153.
66. Nunes, V.; Silva, F.J.G.; Andrade, M.F.; et al. Increasing the lifespan of high-pressure die cast molds subjected to severe wear. *Surf. Coat. Technol.* **2017**, *332*, 319–331.
67. Vereschaka, A.; Kataeva, E.; Sitnikov, N.; et al. Influence of Thickness of Multilayered Nano-Structured Coatings Ti-TiN-(TiCrAl)N and Zr-ZrN-(ZrCrNbAl)N on Tool Life of Metal Cutting Tools at Various Cutting Speeds. *Coatings* **2018**, *8*, 44.
68. Momeni, S.; Tillmann, W. Investigation of the self-healing sliding wear characteristics of NiTi-based PVD coatings on tool steel. *Wear* **2016**, *368*, 53–59.
69. Hu, N.; Khan, M.; Wang, Y.; et al. Effect of Microstructure on the Thermal Conductivity of Plasma Sprayed Y_2O_3 Stabilized Zirconia (8% YSZ). *Coatings* **2017**, *7*, 198.
70. Kim, M.; Kim, S.; Kim, T.; et al. Mechanical and thermal properties of epoxy composites containing zirconium oxide impregnated halloysite nanotubes. *Coatings* **2017**, *7*, 231.
71. Maity, S. Optimization of processing parameters of in-situ polymerization of pyrrole on woollen textile to improve its thermal conductivity. *Prog. Org. Coat.* **2017**, *107*, 48–53.
72. Krella, A. Resistance of PVD Coatings to Erosive and Wear Processes: A Review. *Coatings* **2020**, *10*, 921.
73. Duminica, F.D.; Belchi, R.; Libralesso, L.; et al. Investigation of Cr(N)/DLC Multilayer Coatings Elaborated by PVD for High Wear Resistance and Low Friction Applications. *Surf. Coat. Technol.* **2018**, *337*, 396–403.
74. Meier, S.M.; Gupta, D.K. The Evolution of Thermal Barrier Coatings in Gas Turbine Engine Applications. *J. Eng. Gas Turbine Power* **1994**, *116*, 250–257.
75. Ferreira, A.A.; Silva, F.J.G.; Pinto, A.G.; et al. Characterization of Thin Chromium Coatings Produced by PVD Sputtering for Optical Applications. *Coatings* **2021**, *11*, 215.
76. Sun, Z.; He, G.; Meng, Q.; et al. Corrosion Mechanism Investigation of TiN/Ti Coating and TC4 Alloy for Aircraft Compressor Application. *Chin. J. Aeronaut.* **2020**, *33*, 1824–1835.
77. Natrayan, L.; Balaji, S.; Bharathiraja, G.; et al. Experimental Investigation on Mechanical Properties of TiAlN Thin Films Deposited by RF Magnetron Sputtering. *J. Nanomater.* **2021**, *2021*, 5943486.

78. Singh, J.; Wolfe, D.E. Review Nano and Macro-Structured Component Fabrication by Electron Beam-Physical Vapor Deposition (EB-PVD). *J. Mater. Sci.* **2005**, *40*, 1–26.
79. Kapopara, J.M.; Mengar, A.R.; Chauhan, K.V.; et al. Modelling and Analysis of Sputter Deposited ZrN Coating by CFD. In Proceedings of the IConAMMA 2016 International Conference on Advances in Materials and Manufacturing Applications, Bangalore, India, 14–16 July 2016; p. 012205.
80. Moll, E.; Bergmann, E. Hard Coatings by Plasma-Assisted PVD Technologies: Industrial Practice. *Surf. Coat. Technol.* **1989**, *37*, 483–509.
81. Silva, F.J.G.; Baptista, A.P.M.; Pereira, E.; et al. Microwave plasma chemical vapour deposition diamond nucleation on ferrous substrates with Ti and Cr interlayers. *Diam. Relat. Mater.* **2002**, *11*, 1617–1622.
82. Sousa, V.F.C.; Fernandes, F.; Silva, F.J.G.; et al. Wear Behavior Phenomena of TiN/TiAlN HiPIMS PVD-Coated Tools on Milling Inconel 718. *Metals* **2023**, *13*, 684.
83. Fernandes, F.; Calderon, V.; Ferreira, P.J.; et al. Low peak power deposition regime in HiPIMS: Deposition of hard and dense nanocomposite Ti-Si-N films by DOMS without the need of energetic bombardment. *Surf. Coat. Technol.* **2020**, *397*, 125996.
84. Rajput, S.; Gangopadhyay, S.; Fernandes, F.; et al. Influence of Ag additions on the structure, mechanical properties and oxidation behaviour of CrAlNAg coatings deposited by sputtering. *Surf. Coat. Technol.* **2021**, *426*, 127767.
85. Sousa, V.F.C.; Silva, F.J.G.; Lopes, H.; et al. Wear Behavior and Machining Performance of TiAlSiN-Coated Tools Obtained by dc MS and HiPIMS: A Comparative Study. *Materials* **2021**, *14*, 5122.
86. Sousa, V.F.C.; Silva, F.J.G.; Alexandre, R.; et al. Experimental study on the wear evolution of different PVD coated tools under milling operations of LDX2101 duplex stainless steel. *Adv. Manuf.* **2023**, *11*, 158–179.
87. Sousa, V.F.C.; Castanheira, C.; Silva, F.J.G.; et al. Wear Behavior of Uncoated and Coated Tools in Milling Operations of AMPCO (Cu-Be) Alloy. *Appl. Sci.* **2021**, *11*, 7762.
88. Galán-Martínez, A.D.; Santiago-Alvarado, A.; González-García, J.; et al. Analysis and Design of a Mechanical System to Use with the Ronchi and Fizeau Tests. In Proceedings of the 8th Iberoamerican Optics Meeting and 11th Latin American Meeting on Optics, Lasers, and Applications, Porto, Portugal, 22–26 July 2013; Volume 8785, p. 87851Z.
89. Ponte, F.; Sharma, P.; Figueiredo, N.M.; et al. Decorative Chromium Coatings on Polycarbonate Substrate for the Automotive Industry. *Materials* **2023**, *16*, 2315.
90. Skordaris, G.; Bouzakis, K.; Kotsanis, T.; et al. Effect of PVD film's residual stresses on their mechanical properties, brittleness, adhesion and cutting performance of coated tools. *CIRP J. Manuf. Sci. Technol.* **2017**, *18*, 145–151.
91. Silva, F.J.G.; Fernandes, A.J.S.; Costa, F.M.; et al. Tribological behavior of CVD diamond films on steel substrates. *Wear* **2003**, *255*, 846–853.
92. Damm, D.D.; Contin, A.; Barbieri, F.C.; et al. Interlayers applied to CVD diamond deposition on steel substrate: A review. *Coatings* **2017**, *7*, 141.
93. Trucchi, D.M.; Bellucci, A.; Girolami, M.; et al. Surface texturing of CVD Diamond assisted by ultra short laser pulses. *Coatings* **2017**, *7*, 185.
94. Pinto, G.; Silva, F.J.G.; Baptista, A.; et al. A critical review on the numerical simulation related to physical vapour deposition. *Procedia Manuf.* **2018**, *17*, 860–869.
95. Voottipruex, P.; Bergado, D.T.; Lam, L.G.; et al. Back-analyses of flow parameters of PVD improved soft Bangkok clay with and without vacuum preloading from settlement data and numerical simulations. *Geotext. Geomembr.* **2014**, *42*, 457–467.
96. Kapopara, J.; Mengar, A.; Chauhan, K.; et al. CFD Analysis of Sputtered TiN Coating. *Mater. Today Proc.* **2017**, *4*, 9390–9393.
97. Bobzin, K.; Brinkmann, R.; Mussenbrock, T.; et al. Continuum and kinetic simulations of the neutral gas flow in an industrial physical vapor deposition reactor. *Surf. Coat. Technol.* **2013**, *237*, 176–181.
98. Pinto, G.; Silva, F.; Porteiro, J.; et al. Numerical Simulation Applied to PVD Reactors: An Overview. *Coatings* **2018**, *8*, 410.
99. Skordaris, G.; Bouzakis, K.; Kotsanis, T.; et al. Film thickness effect on mechanical properties and milling performance of nano-structured multilayer PVD coated tools. *Surf. Coat. Technol.* **2016**, *307*, 452–460.
100. Pinto, G.F.; Almeida, D.; Silva, F.J.G.; et al. Correlating Cutting Performance and Surface Roughness under Different Bias Using TiAlTaN Coated Milling Tools. *J. Mech. Eng. Manuf.* **2025**, *1*, 7.
101. Abdullah, M.Z.B.; Ahmad, M.A.; Abdullah, A.N.; et al. Metal release of multilayer coatings by physical vapour deposition (PVD). *Procedia Eng.* **2016**, *148*, 254–260.
102. Shuai, J.; Zuo, X.; Wang, Z.; et al. Comparative study on crack resistance of TiAlN monolithic and Ti/TiAlN multilayer coatings. *Ceram. Int.* **2020**, *46*, 6672–6681.
103. Knotek, O.; Löffler, F.; Krämer, G. Multicomponent and multilayer physically vapour deposited coatings for cutting tools. *Surf. Coat. Technol.* **1992**, *54*, 241–248.

104. Du, H.; Zhao, H.; Xiong, J.; et al. Effect of interlayers on the structure and properties of TiAlN-based coatings on WC-Co cemented carbide substrate. *Int. J. Refract. Met. Hard Mater.* **2013**, *37*, 60–66.
105. Kale, A.N.; Ravindranath, K.; Kothari, D.C.; et al. Tribological properties of (Ti, Al)N coatings deposited at different bias voltages using the cathodic arc technique. *Surf. Coat. Technol.* **2001**, *145*, 60–70.
106. Ürgen, M.; Eryilmaz, O.L.; Çakir, A.F.; et al. Characterization of Molybdenum Nitride Coatings Produced by Arc-PVD Technique. *Surf. Coat. Technol.* **1997**, *94*, 501–506.
107. Romero, E.C.; Macías, A.H.; Nonell, J.M.; et al. Mechanical and tribological properties of nanostructured TiAlN/TaN coatings deposited by DC magnetron sputtering. *Surf. Coat. Technol.* **2019**, *378*, 124941.
108. Martinho, R.P. Revestimentos PVD Mono e Multicamada Para Moldes Utilizados na Injecção de Plásticos Reforçados. Master's Thesis, FEUP, Porto, Portugal, 2009.
109. Barshilia, H.C.; Ananth, A.; Khan, J.; et al. Ar + H_2 plasma etching for improved adhesion of PVD coatings on steel substrates. *Vacuum* **2012**, *86*, 1165–1173.
110. Steimann, P.A.; Hintermann, H.E. Adhesion of TiC and Ti(C, N) coatings on steel. *J. Vac. Sci. Technol. A* **1985**, *3*, 2394–2400.
111. Lente, H.V.; Til, J.I.V. Articulation of sustainability in the emerging field of nanocoatings. *J. Clean. Prod.* **2008**, *16*, 967–976.
112. Biswas, B.; Purandare, Y.; Sugumaran, A.; et al. Effect of Chamber Pressure on Defect Generation and Their Influence on Corrosion and Tribological Properties of HIPIMS Deposited CrN/NbN Coatings. *Surf. Coat. Technol.* **2018**, *336*, 84–91.
113. Gudmundsson, J.T. Physics and Technology of Magnetron Sputtering Discharges. *Plasma Sources Sci. Technol.* **2020**, *29*, 113001.
114. Ghailane, A.; Makha, M.; Larhlimi, H.; et al. Design of Hard Coatings Deposited by HiPIMS and DcMS. *Mater. Lett.* **2020**, *280*, 128540.
115. Geng, D.; Li, H.; Chen, Z.; et al. Microstructure, Oxidation Behavior and Tribological Properties of AlCrN/Cu Coatings Deposited by a Hybrid PVD Technique. *J. Mater. Sci. Technol.* **2022**, *100*, 150–160.
116. Greczynski, G.; Jensen, J.; Böhlmark, J.; et al. Microstructure Control of CrN_x Films during High Power Impulse Magnetron Sputtering. *Surf. Coat. Technol.* **2010**, *205*, 118–130.
117. Dong, X.; Su, Y.; Wu, Z.; et al. Reactive Pulsed DC Magnetron Sputtering Deposition of Vanadium Oxide Thin Films: Role of Pulse Frequency on the Film Growth and Properties. *Appl. Surf. Sci.* **2021**, *562*, 150138.
118. Caliskan, H.; Panjan, P.; Kurbanoglu, C. Hard Coatings on Cutting Tools and Surface Finish. In *Comprehensive Materials Finishing*; Elsevier: Oxford, UK, 2017; Volume 3, pp. 230–242.
119. Man, B.Y.; Guzman, L.; Miotello, A.; et al. Microstructure, oxidation and H_2-permeation resistance of TiAlN films deposited by DC magnetron sputtering technique. *Surf. Coat. Technol.* **2004**, *180–181*, 9–14.
120. Hsieh, J.H.; Liang, C.; Yu, C.H.; et al. Deposition and characterization of TiAlN and multi-layered TiN/TiAlN coatings using unbalanced magnetron sputtering. *Surf. Coat. Technol.* **1998**, *108–109*, 132–137.
121. Mitsuo, A.; Uchida, S.; Nihira, N.; et al. Improvement of high-temperature oxidation resistance of titanium nitride and titanium carbide films by aluminum ion implantation. *Surf. Coat. Technol.* **1998**, *103–104*, 98–103.
122. Yang, K.; Xian, G.; Zhao, H.; et al. Effect of Mo content on the structure and mechanical properties of TiAlMoN films deposited on WC–Co cemented carbide substrate by magnetron sputtering. *Int. J. Refract. Met. Hard Mater.* **2015**, *52*, 29–35.
123. Tomaszewski, Ł.; Gulbiński, W.; Urbanowicz, A.; et al. TiAlN-based wear resistant coatings modified by molybdenum addition. *Vacuum* **2015**, *121*, 223–229.
124. Yi, J.; Chen, S.; Chen, K.; et al. Effects of Ni content on microstructure, mechanical properties and Inconel 718 cutting performance of AlTiN-Ni nanocomposite coatings. *Ceram. Int.* **2018**, *45*, 474–480.
125. Liu, Z.R.; Chen, L.; Du, Y.; et al. Influence of Ru-addition on thermal decomposition and oxidation resistance of TiAlN coatings. *Surf. Coat. Technol.* **2020**, *401*, 126234.
126. Aninat, R.; Valle, N.; Chemin, J.-B.; et al. Addition of Ta and Y in a hard Ti-Al-N PVD coating: Individual and conjugated effect on the oxidation and wear properties. *Corros. Sci.* **2019**, *156*, 171–180.
127. Chandra, N.G.P.S.; Otsuka, Y.; Mutoh, Y.; et al. Effect of coating thickness on fatigue behavior of TiAlN coated Ti-alloys. *Int. J. Fatigue* **2020**, *140*, 105767.
128. Das, S.; Guha, S.; Ghadai, R.; et al. A comparative analysis over different properties of TiN, TiAlN and TiAlSiN thin film coatings grown in nitrogen gas atmosphere. *Mater. Chem. Phys.* **2021**, *258*, 123866.
129. Hogmark, S.; Jacobson, S.; Larsson, M. Design and evaluation of tribological coatings. *Wear* **2000**, *246*, 20–33.
130. Zhang, M.; Cheng, Y.; Xin, L.; et al. Cyclic oxidation behaviour of Ti/TiAlN composite multilayer coatings deposited on titanium alloy. *Corros. Sci.* **2020**, *166*, 108476.
131. Çomakli, O. Improved structural, mechanical, corrosion and tribocorrosion properties of Ti45Nb alloys by TiN, TiAlN monolayers, and TiAlN/TiN multilayer ceramic films. *Ceram. Int.* **2021**, *47*, 4149–4156.
132. Liu, Y.; Yu, S.; Shi, Q.; et al. Multilayer Coatings for Tribology: A Mini Review. *Nanomaterials* **2022**, *12*, 1388.
133. Sun, Y.D.; Yan, J.Y.; Zhang, S.; et al. Influence of modulation periods and modulation ratios on the structure and mechanical properties of nanoscale TiAlN/TiB2 multilayers prepared by IBAD. *Vacuum* **2012**, *86*, 949–952.

134. Shugurov, A.R.; Kazachenok, M.S. Mechanical properties and tribological behavior of magnetron sputtered TiAlN/TiAl multilayer coatings. *Surf. Coat. Technol.* **2018**, *353*, 254–262.
135. Silva, F.J.G.; Fernandes, A.J.S.; Costa, F.M.; et al. A new interlayer approach for CVD diamond coating of steel substrates. *Diam. Relat. Mater.* **2004**, *13*, 828–833.
136. Shang, H.; Li, J.; Shao, T. Mechanical properties and thermal stability of TiAlN/Ta multilayer film deposited by ion beam assisted deposition. *Appl. Surf. Sci.* **2014**, *310*, 317–320.
137. Zhao, F.; Ge, Y.; Wang, L.; et al. Tribological and mechanical properties of hardness-modulated TiAlSiN multilayer coatings fabricated by plasma immersion ion implantation and deposition. *Surf. Coat. Technol.* **2020**, *402*, 126475.
138. Baptista, A.; Pinto, G.F.; Sousa, V.F.C.; et al. Studying the Machining Performance of DSS Steel Using Single and Multilayered TiAlSiN Coated Tools Deposited by HiPIMS. In *Flexible Automation and Intelligent Manufacturing: Establishing Bridges for More Sustainable Manufacturing Systems, Proceedings of the FAIM 2023, Porto, Portugal, 18–22 June 2023*; Silva, F.J.G., Pereira, A.B., Campilho, R.D.S.G., Eds.; Springer Nature: Cham, Switzerland, 2024.
139. Bonu, V.; Jeevitha, M.; Kumar, V.P.; et al. Solid particle erosion and corrosion resistance performance of nanolayered and multilayered Ti/TiN and TiAl/TiAlN coatings deposited on Ti6Al4V. *Surf. Coat. Technol.* **2020**, *387*, 125531.
140. Wang, J.; Yazdi, M.A.P.; Lomello, F.; et al. Influence of microstructures on mechanical properties and tribology behaviors of TiN/TiAlN multilayer coatings. *Surf. Coat. Technol.* **2016**, *20*, 441–446.