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Review

Characteristics and Wear Mechanisms of TiAlN-Based Coatings for Machining Applications: A Comprehensive Review

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Abstract: The machining process is still a very relevant process in today's industry, being used to produce high quality parts for multiple industry sectors. The machining processes are heavily researched, with the focus on the improvement of these processes. One of these process improvements was the creation and implementation of tool coatings in various machining operations. These coatings improved overall process productivity and tool-life, with new coatings being developed for various machining applications. TiAlN coatings are still very present in today's industry, being used due to its incredible wear behavior at high machining speeds, high mechanical properties, having a high-thermal stability and high corrosion resistance even at high machining temperatures. Novel TiAlN-based coatings doped with Ru, Mo and Ta are currently under investigation, as they show tremendous potential in terms of mechanical properties and wear behavior improvement. With the improvement of deposition technology, recent research seems to focus primarily on the study of nanolayered and nanocomposite TiAlN-based coatings, as the thinner layers improve drastically these coating's beneficial properties for machining applications. In this review, the recent developments of TiAlN-based coatings are going to be presented, analyzed and their mechanical properties and cutting behavior for the turning and milling processes are compared.

Keywords: machining; milling; turning; tool coating; TiAlN; TiAlN-based coatings; multilayer; nanolayer; wear mechanisms

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Citation: Sousa, V.F.C.; Da Silva, F.J.G.; Pinto, G.F.; Baptista, A.; Alexandre, R. Characteristics and Wear Mechanisms of TiAlN-Based Coatings for Machining Applications: A Comprehensive Review. *Metals* **2021**, *11*, 260. https://doi.org/10.3390/met11020260

Academic Editor: Emin Bayraktar

Received: 31 December 2020
Accepted: 29 January 2021
Published: 4 February 2021

1. Introduction

Machining remains a very important process, with the machining industry in continuous growth in recent years, and still having a considerable expected growth in the following years. The turning and milling process are the most used machining processes; however, the drilling process is quite relevant for the machining industry as well. This importance of the machining processes is based on the high demand for high-quality and complex parts for various industry applications such as, the aeronautical and the aerospace industries [1,2]. These two industries benefit specially from the machining process, as it can produce highly complex parts accurately, by employing 5-axis machining methods or even 6-axis machining methods, enabling the complete production of complex parts, from the raw material to the final part, without the need to stop [3,4]. The need for these types of parts also creates the need for process improvement, by reducing machining times, improving tool-life or by applying new machining methods. These topics are still researched recently, with many being focused on the tool used for the machining process, as the tool directly influences the machining process's productivity, with studies being made on the creation of new and improved tool designs, such as the study performed by

Siddiqui et al. [5], where the development of a self-lubricated textured tool and its employment in the dry turning of aluminum alloy Al6061- T6 is described. The textured cutting tool allowed for the use of MoS_2 as a solid lubricant. It was found that this novel design significantly reduced the wear of the tool (by up to 35%), and also, the cutting temperature was reduced by up to 40% when compared to turning with the conventional tool under dry machining conditions. Still regarding the development of new tools and methods, there have also been improvements regarding the cemented carbide tools used, for example, gradient carbide tools [6] (with different layers with different values of hardness) have been developed. This enables one to tailor the base tool (uncoated substrate) to a certain machining application, conferring the tool with increased wear resistance. There have been some studies conducted on this topic, such as this study performed by Zhou et al. [7] where various gradient cemented carbides (coated and uncoated) are tested in machining tests of a titanium alloy. It was found that the gradient's layer thickness influences the cutting performance and that this thickness can be altered by changing the composition of the cemented carbide itself. Moreover, the tool with thicker layers exhibited the best cutting performance, suffering less wear damage. This is a very interesting study, as the base tool offers a better set of properties (compared to normal cemented carbide tools) that, when combined with a tool coating, will improve even further the tool's performance. Tool coatings have greatly contributed to the machining sector since they were first developed, but there is still room for improvement in this area and thus, recent studies made on machining tools also focus on the employment of coatings to machine certain materials, especially titanium alloys [8], aluminum alloys (these aluminum alloys are primarily applied to the aerospace and aeronautical industry, with some applications in the automotive industry) [9,10] and hard-to-machine materials such as Inconel [11], given that these materials are heavily used in the production of parts for the aeronautical industry. These studies are very important as they provide valuable information on what coatings are best suited for machining a certain material, or which coating to use when wanting to optimize the machining process [2,12].

Machining tools that are employed in today's machining processes are usually coated tools, either solid coated tools, machining tools with coated inserts, or just coated inserts in the case of the turning process. The use of coated tools has greatly improved the machining processes, enabling the machining of materials at higher speeds, when compared to regular uncoated tools and inserts (steel and solid carbide tools) [13–15]. These coatings have proved to be especially useful when it comes to improving tool-life and overall tool performance, when machining materials with low machinability [16,17]. This is due to the improvement of the mechanical properties of the tool by the coating, such as increased hardness, oxidation resistance, toughness, thermal stability (ability to retain microstructure at higher temperatures) and reduced friction coefficient. The employment of tool coatings also contributes for a better surface quality of the machined part [18] and reduction of the cutting forces developed during the machining process (especially due to reduction in friction coefficient), still a very important aspect in today's research of these cutting processes [19]. However, regarding tool-tip temperature and machining temperature, it has been reported that coated tools usually experience higher machining temperatures than uncoated tools [20]. Yet this fact does not seem to negatively impact the coated tool's life (in most cases), since there are other factors that occur at the tool-chip interface, such as the formation of a coating oxidation layer. Moreover, coatings can be tailored to fit a certain application, and the introduction of multiple layers influences the coating's properties [21]. These factors contribute to the tool's life, with coated tools exhibiting overall less wear when compared to uncoated tools, with numerous studies being conducted about this topic. For example, in the study performed by Thakur et al. [22], the performance of uncoated chemical vapor deposition (CVD) $TiCN/Al_2O_3$ bilayer and physical vapor deposition (PVD) TiAlN/TiN multilayer coated tools was evaluated. These tools were employed in the turning of Incoloy 825 at three different cutting speeds (51, 84 and 124 m/min). The coated tools outperformed the uncoated tools, however, this margin increased for the higher cutting speed values. Coated tools produced a better surface finish on the part when compared to the uncoated tools, furthermore, the PVD coatings suffered overall less wear than the CVD coating, exhibiting the lowest value for friction coefficient of all the tools (coated and uncoated). Regarding tool life, coatings improved greatly in this aspect, with the uncoated tools lasting only 90 s, and the CVD and PVD tool lasting for 28 and 40 min, respectively. Studies such as these are very important for the optimization of machining processes, providing valuable information regarding coating application and material machinability. Moreover, studies such as these highlight the value that tool coatings have when employed in machining processes, especially in improving tool-life and part production quality.

Coatings are usually obtained by two different processes, either by CVD or by PVD, with some differences between the two processes [23]. The CVD deposition process was the first to be invented, being used then for the deposition of TiN and TiC coatings in the 1960s, as a response to the tool life problem, then present in the machining industry. CVD produces coatings by having a precursor pumped inside of a reactor (the flux of this precursor is regulated by valves). The precursor molecules pass by the substrate (placed inside the reactor) and are deposited on its surface, giving origin to a thin hard film that has a relatively uniform thickness throughout the substrate's surface. The working temperature of this process is quite high, reaching temperatures of up to 900 °C. The PVD process was developed after the CVD, having some advantages when compared to it, such as a lower deposition temperature and the ability to create different types of coating (such as the TiAlN coating, created as an improvement over the TiN coating). The first coating deposited by this technique was TiN coating, achieved in the 1970s [24]. PVD consists of various methods, such as evaporation, sputtering and molecular beam epitaxy (MBE). Regarding sputtering, the coating is achieved by placing a magnetron near the target (containing the elements that are going to be part of the coating), in a vacuum reactor chamber. An inert gas is then introduced in the chamber, then a high voltage is applied between the target and the substrate also placed inside the reactor chamber, causing the release of atomic size particles from the target. These particles are projected onto the substrate, causing the formation of a thin solid film. In the evaporation technique, however, the target itself acts as an evaporation source, while the sample's material works as a cathode, the target material is heated at a high vapor pressure, which causes particle to release and be dispersed inside de reactor. The gas that is being pumped inside the chamber clashes with these particles, causing their acceleration, which in turn creates a plasma that will be deposited onto the substrate's surface. This process, contrary to the CVD process, runs at a much lower temperature, under 500 °C. Thus, PVD obtained coatings can be deposited onto steel substrate and cemented carbide tools without negatively impacting the properties of these types of substrate. Furthermore, the PVD process does not involve the use of any toxic precursors, unlike the CVD process, and is more energy efficient, having a considerably lower energy consumption than the CVD process [25,26].

Choosing the right coating deposition method is very important, as seen in the previous paragraph. Different techniques confer the coatings with different properties, being increased mechanical properties, adhesion properties and even residual stresses. Both CVD and PVD methods have certain advantages and disadvantages, for example, CVD coatings are very difficult to deposit onto steel substrates, due to high deposition temperature. However, there have been studies that seek to solve this problem, by implementing an interlayer, between the coating and the substrate, that will protect the substrate during the deposition of the outer coating [27,28]. Regarding the PVD process, due to its deposition temperatures, usually, good adhesive strength of coatings can be achieved when these are deposited onto steel substrates [29]; however, this process is a line-of-sight process, which means that coating deposition on complex geometries is considerably harder when compared to CVD. Moreover, the control of the thickness throughout the substrates surface is also harder. These problems can be attenuated by using a different PVD process, such as pulsed high-power sputtering [30]. However, this can come at a cost, such as inducing excessive residual stresses in the coating or even sacrificing adhesive strength. These two deposition processes (CVD and PVD) also influence machining performance, for example, PVD coatings are usually thinner than CVD coatings, however, there are some studies that report coatings with thicknesses up to 15 µm [31]. This coupled with the fact that PVD coatings exhibit compressive stresses, makes the cutting edge of the coated tool a very strong and resistant edge, making these types of coatings ideal for finishing operations, whereas in the case of CVD coatings, these exhibit tensile residual stresses and are usually thicker, making them more suited for roughing operations where, for example, a high material removal rate is preferred [32–34]. The control over these coatings properties makes them very versatile, moreover, they can be specifically made for a certain application, experiencing various combinations of coating's structures and compositions. Coatings are not only used on tools for metal cutting operations [35,36], their mechanical properties, high wear resistance, high temperature resistance and high corrosion resistance makes them very appealing for a wide range of applications. For example, they have seen some recent use in wood cutting processes [37], medical applications [38], mold industry [39], automotive (especially for brake pads) [40] and even being deposited in alloys used for nuclear fuel cladding [41,42].

As previously mentioned, the PVD process involves various methods for the deposition of coatings. These methods influence not only coating composition, but their properties as well. These methods are primarily divided into two groups: sputtering and evaporation. All these methods can be observed in Figure 1.

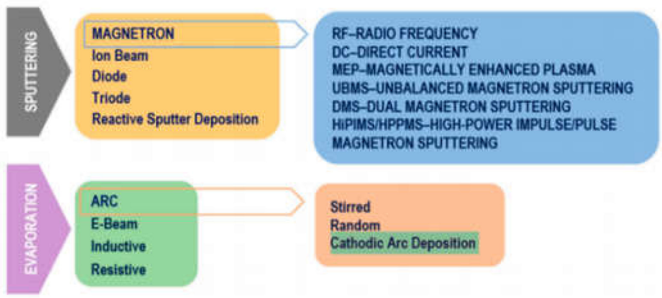

Figure 1. Physical vapor deposition (PVD) techniques currently being used in the production and deposition of coatings [27].

Currently, the most used method to produce PVD coatings is the direct current method (DC) for magnetron sputtering; however, there seems to be a shift in the use of these techniques to ones such as, unbalanced magnetron sputtering (UBMS) [25,26] and the high-power impulse/pulse magnetron sputtering (HiPIMS/HPPMS), the latter rising in popularity in recent years. There are several studies conducted regarding these deposition techniques, as they confer the coating with different properties, more suited to certain applications. For example, in the study carried out by Romero et al. [43], an evaluation of microstructure and tribological performance of TiAlTaN-(TiAlN/TaN) coatings has been observed. Various coatings of this type were deposited onto AISI M2 steel, the deposition consisted of a first layer of TiAlN/TaN followed by a second layer of TiAlTaN. In total, four combinations with different volume fractions for each layer were tested. Furthermore, the deposition was achieved by DC sputtering using two magnetrons and two targets, and by controlling the substrate rotation speed. The authors were able to control the coating's architecture, and thus their mechanical properties, by varying the rotation speed of the substrate during deposition. They were able to find the best values for the volume fractions of each layer, concluding that the combination of 48% TiAlTaN and 52% of TiAlN/TaN exhibited the best balance between adhesion properties, hardness (29 GPa) and friction coefficient (0.68). Recently, there have been some studies highlighting the benefit of some deposition techniques such as HiPIMS, linking this technique with an increase in mechanical properties and a betterment of adhesion properties. Zauner et al. [44] studied the influence of the HiPIMS parameter choice in the properties of TiAlN films, by using a TiAl composite target in mixed Ar/N_2 atmospheres. The parameters in question were the pulse frequency and duration, the N_2 flow ratio, target composition and substrate bias voltage. The authors found that changing these parameters has a great influence on the final coating's properties, even enabling the control of the coating's structure. The authors claim to obtain hardness of the TiAlN coating of up to 36 GPa. Still regarding the influence of deposition parameters in the coating's properties, in the work performed by Zhao et al. [45] the influence of the bias voltage chosen during deposition of TiAlN coatings is evaluated. Coatings have been fabricated using a multi-arc ion plating device. Various values for this parameter were tested, the lowest value of bias voltage being −40 V and the highest value being −120 V. The lowest value produced the coating with superior toughness, being the most suited for cutting applications. Increasing the bias voltage resulted in a loss of toughness, however, there was an increase in hardness and plasticity. Choosing the right deposition technique is of great importance when fabricating a tool coating. Thus, there have been some studies whose compare some of these techniques in the deposition of tool coatings, as seen in the study presented by Tillman et al. [46] where a comparison between DCMS (Direct Current Magnetron Sputtering) and HiPIMS in the deposition of TiAlN and TiAlN/TiAlCN coatings is made. The films were deposited in heat-treated AISI H11 steel, and the samples were evaluated regarding wear resistance and residual stresses. The authors found that the coatings obtained by HiPIMS had significantly higher residual stresses than the DCMS coatings. Furthermore, the adhesion of the coatings obtained by DCMS was higher. However, the TiAlN coatings deposited by HiPIMS displayed higher wear resistance than the other coatings obtained by DCMS. The problems presented in the last study have been researched as well, with some solutions for the adhesion problems and the higher compressive stresses of HiPIMS coatings being presented, such as the use of substrate surface texturing methods using etching process, which can help increasing the coating's adhesion and relieve excessive compressive stresses [47]. There are also some very recent studies on a novel deposition technique that can produce high ionization rates like the HiPIMS method. This method is the Continuous High-Power Magnetron Sputtering (C-HPMS). Liu et al. [48] studied TiAlN coatings obtained by this technique. The authors were able to obtain a coating with a very high hardness value (34.4 GPa) and a good adhesive strength (75 N). Moreover, the deposited coating presented very few particles on its surface. The method described in this paper paves the way to obtain droplet-free coatings and good mechanical properties by employing this method, presenting benefits such as fast deposition rate and efficient ionization.

Evaporation methods are seeing some recent research as well, with DC arc evaporation being the most common technique among them. However, some attention is being given to the cathodic arc deposition method, with studies being made relating deposition method and parameters to the coating's overall properties [49], even relating rotation speed during deposition and substrate orientation to the mechanical properties of deposited coatings [50], such as the study previously presented [43]. However, this deposition technique is being recently used mostly for the deposition and synthetization of borides and borides-related coatings, which are unable to be obtained by DC arc evaporation [49,51].

Regarding coating characterization as it was previously mentioned, coatings can be designed in order to fit a certain application, by controlling its architecture and composition, and thus, its microstructure and mechanical properties. There are various different coating designs applied to substrates for a wide range of applications. These can be observed in Figure 2.

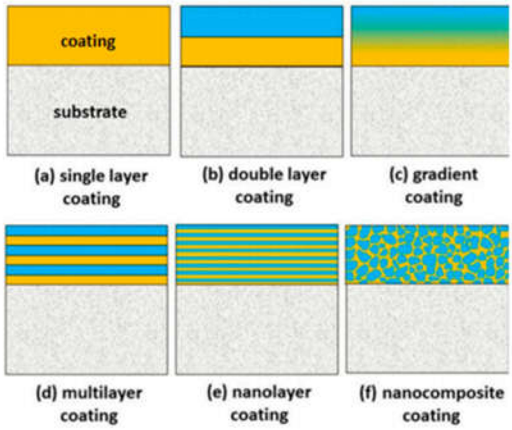

Figure 2. Different types of coating structure commonly applied to substrates [24].

The coatings can be identified as follows:

a. Monolayer (single layer) coating;
b. Bilayer (double layer) coating;
c. Gradient coating;
d. Multilayer coating;
e. Nanolayer coating;
f. Nanocomposite coating.

Different types of coating structure are chosen to deal with different kinds of problems, for example, the use of a multilayer coating can improve significantly upon the properties of the single layer coated tool. For example, a multilayered coating has significantly more crack propagation resistance than a single layered coating. The number of layers contributes to this, furthermore, an increase in the number of layers will also increase properties such as hardness [24,52,53]. A scheme of how crack propagation usually behaves depending on coating structure can be observed in Figure 3.

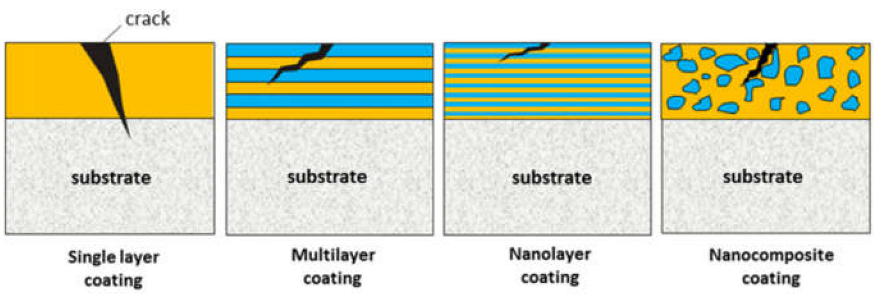

Figure 3. Crack propagation behavior for each of the common coating structure [24].

Layers can also be added to improve adhesion properties, enabling that the deposition of the outer layer, usually the "work" layer, with high adhesive strength. Usually this is done when the outer layer has problems with adhesion to the substrate. Coatings are also characterized by their chemical composition. The elements that constitute the coating confer it with different properties, as certain elements can improve properties such as, corrosion resistance, wear resistance and even thermal conductivity. For example, the first coatings (TiN) were improved by the addition of aluminum, creating the TiAlN coating. This coating proved itself to be very useful in high-speed machining application, being widely employed in many machining applications to this day, because they present an oxide layer created between the tool–workpiece interface, thus conferring this coating with high oxidation resistance [54–57]. Still regarding coating characterization, these are also characterized by their microstructure. Different coatings have different types of microstructure, depending on the deposition method, composition and their architecture, as described in the paper developed by Du et al. [58], where the effect of interlayers of Cr and Ti on the structure of TiAlN based coatings is studied. The authors deposited four types of coatings onto cemented carbide substrates, these being Cr/(Ti,Si,Al)N; Ti/(Ti,Si,Al)N; Cr/TiAlN; and Ti/TiAlN. It was found that the presence of these interlayers influenced the microstructure of the coatings. The Cr interlayer affects the growth of TiAlN based coatings, with the structure of the coatings containing this interlayer exhibiting a mix between columnar crystal morphology and equiaxed crystal morphology. In the case of Ti interlayer, the morphology was columnar. The Cr interlayer also promoted a better adhesion of the TiAlN based coatings onto it.

In this review paper the properties of TiAlN based coatings are going to be evaluated and presented, based on the information collected from recent articles conducted on this topic. The various types of coatings are going to be presented in the subsequent sections, mentioning in more detail these coating's properties such as, structure, microstructure and composition and its influence on the coating's mechanical properties, especially hardness values and young's modulus values. Moreover, the recent applications of these TiAlN based coatings in machining are going to be analyzed, highlighting the coating's performance on the various machining process (primarily turning and milling). Still regarding coating performance in machining, the wear mechanisms that these coatings suffer are also going to be analyzed and compared between each-other, as the analysis of these wear mechanisms gives very valuable information regarding the optimization and improvement of these machining processes [39,43]. This review intends to fill an existing gap about structured information regarding TiAlN-based coatings utilized in machining tools, mainly based on the most recent developments published in this field. This information, regarding wear behavior and the mechanical properties of the coatings, is going to be presented under the form of tables in order to convey a clear and easy-to-read message. Furthermore, the various types of structure of TiAlN-based coatings were divided into sections, with a section for monolayered, multilayered and nanolayered TiAlN-based coatings being created.

2. TiAlN-Based Coatings

Since its development in the 1970s, the TiAlN coating offered a great opportunity for enhancing tool life and performance for high-speed machining applications. Due to its properties, TiAlN and TiAlN-based coatings are still among the most used coatings for machining applications today, making them a very appealing research matter, with many new coatings being tested and evaluated for a wide variety of machining applications. Furthermore, recent studies also focus on the influence of new doping elements in the properties of TiAlN-based coatings.

In this chapter, recent developments made on TiAlN-based coatings are going to be presented, namely:

- The studies being conducted about monolayered TiAlN-based coatings, mentioning the influence of doping elements (such as, Ru, Ta, Y and Mo) on the overall properties of these coatings;
- Studies about multilayered coatings, presenting the new structures and composition combination which are being employed recently and analyzing its influence on the coating's properties;
- Studies being conducted about nanolayered coatings, mentioning the recent developments being made on this topic, presenting the various structures and their benefits when compared to the other types of TiAlN-based coatings.

In total, three coating types are going to be divided into subsections inside this section. Additionally, the information regarding these coating's mechanical properties, especially Hardness and Young's Modulus values, are going to be presented in a subsection for each of the coating types. The wear mechanisms that these coatings suffer for various machining applications are also presented, mentioning the wear behavior of these types of coatings and presenting the obtained values for tool life based on the information provided by the various analyzed articles.

2.1. Monolayered TiAlN-Based Coatings

Regarding monolayered TiAlN-based coatings, recent research has been made on the effects on the coating properties of doping TiAlN coatings with certain elements. It has been found that the addition of certain elements to the coating can improve properties such as corrosion resistance and wear behavior. Additionally, the addition of these elements is also linked to an improvement in mechanical properties such as hardness and Young's Modulus. In the study performed by Yang et al. [59], the influence of Mo content on TiAlMoN films is presented. The authors have produced five types of TiAlMoN coatings, varying the amounts of Mo. Composition of the samples used in this work can be observed in Table 1.

Table 1. Chemical composition of the TiAlMoN coatings developed in the work presented by Yang et al. [59].

Sample ID	Composition (at. %)			
	Ti	Al	Mo	N
S1	27.6	24.1	2.8	45.6
S2	23.9	22.2	6.9	47.0
S3	17.8	18.0	8.3	54.9
S4	18.2	19.4	10.1	54.4
S5	16.4	16.7	12.1	54.8

The authors analyzed these coatings determining the mechanical properties for each one of the produced samples. Furthermore, the microstructure of each of the TiAlMoN films was analyzed. It was noticed that the hardness and Young's Modulus increased with the addition of Mo, reaching peak levels of hardness for 12.1% Mo content (S5), concretely, and 50 GPa and 610 GPa for hardness and Young's Modulus value, respectively.

Authors registered the influence of the Mo content on the microstructure, by obtaining SEM images of the coating's cross-section. This phenomenon can be observed in the following images, starting with Figure 4, depicting the film's structure with a Mo content of 2.8 at. % (a) and 6.9 at. % (b).

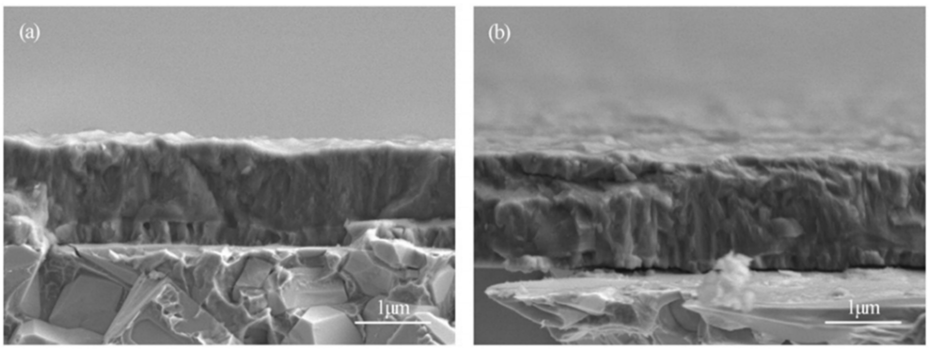

Figure 4. SEM cross-section of the TiAlMoN films with differing Mo contents: 2.8 at. % (**a**); 6.9 at. % (**b**), presented by Yang et al. [59].

It can be observed that at low Mo contents, the structure presents some columnar grains, however, it is not yet uniform. This uniformization was registered at a Mo content of 8.3 at.%. This can be observed in Figure 5.

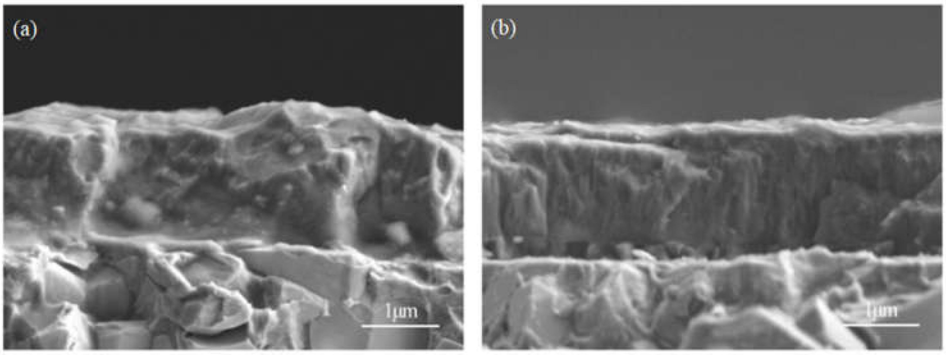

Figure 5. SEM cross-section of the TiAlMoN films with differing Mo contents: 8.3 at. % (**a**); 10.1 at. % (**b**), presented by Yang et al. [59].

There is a change in the film's structure at 10.1 at. % of Mo content, the film's structure starts becoming columnar, finally becoming fully columnar at a Mo content of 12.1 at.%. The latter structure exhibited face-centered cubic TiN-based phases with a preferred orientation. The film's structure with a 12.1 at. % Mo content is displayed in Figure 6.

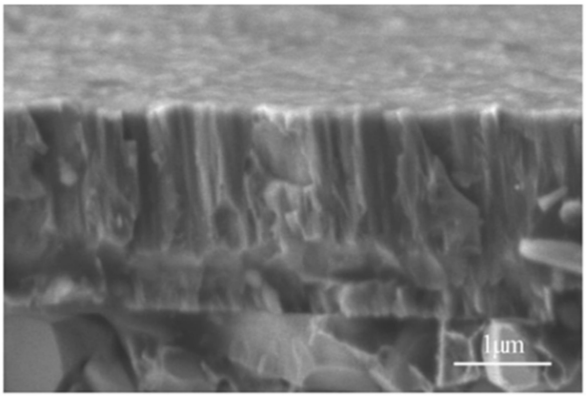

Figure 6. SEM cross-section of the TiAlMoN films with differing Mo contents: 12.1 at. %, presented by Yang et al. [59].

The addition of Mo can also improve the wear behavior of the coating, however, the wear behavior of the TiAlMoN films did not increase with the Mo content, as seen for the mechanical properties. The coating's that exhibited the best wear behavior was the S3 coating, with a Mo content of 8.3 at. %. This is based on the toughness and mechanical properties of the film. One way to evaluate the wear performance of the film is by the analysis of the H/E (Hardness/Young's Modulus) ratio. This ratio can be related to the film's toughness; however, it provides information regarding the plastic deformation of the film (with high H/E ratio values being tied to high plastic deformation resistance). The S3 coating displaying the highest value for this ratio, among all the other TiAlMoN coatings. Still regarding the influence of Mo addition to TiAlN-based coatings, the work presented by Tomaszewski et al. [60] also evaluated the influence of the addition of this element, concluding that the addition of this element is linked to an improvement of mechanical properties. Indeed, a small addition of up to 7.7 at. % allowed to report a significant improvement on the wear behavior of the coating. The authors also registered an improvement on the corrosion resistance properties of the coating, observing that the coating exhibited an improved resistance to pitting corrosion.

The addition of Nickel to TiAlN-based coatings is also an interesting topic. Similar to Mo, the addition of Ni to coatings also has an influence on the microstructure, as reported by Yi et al. [61] in their study, where three samples of AlTiN-Ni with differing contents of Ni are analyzed and subsequently tested in the turning of Inconel 718. The analyzed AlTiN-Ni coatings had 0%, 1.5% and 3% Ni. The AlTiN-Ni coatings were obtained via PVD cathodic arc evaporation. Figure 7 shows the three cross-sectional images of the coatings.

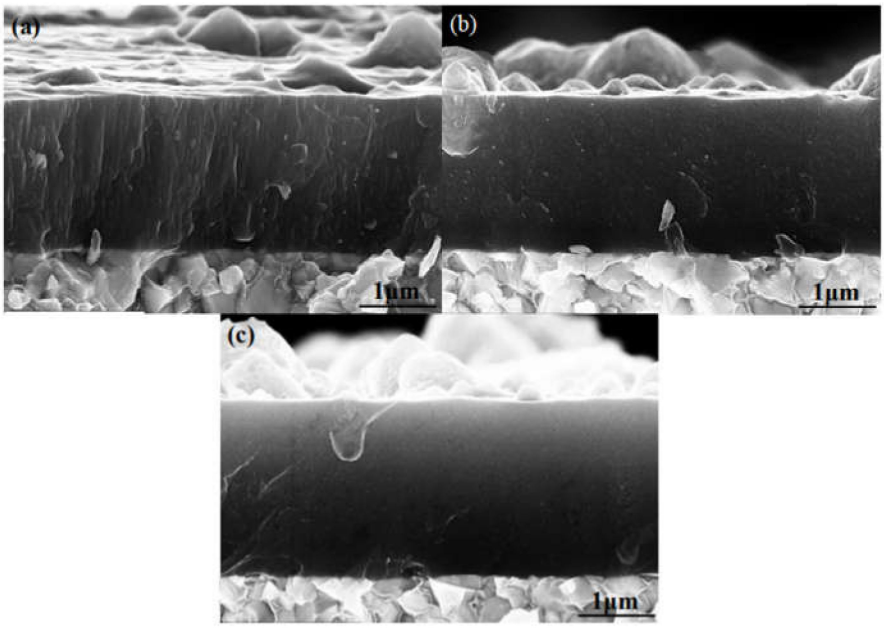

Figure 7. AlTiN-Ni coatings with differing Ni contents: 0% (**a**); 1.5% (**b**); 3% (**c**), presented by Yi et al. [61].

There is an evident change in microstructure depending on the Nickel content. Observing Figure 7a, the microstructure of the AlTiN-Ni coating is columnar. However, it can be noted that the addition of Ni promotes a homogenization of the structure (nanocrystalline structure). The authors registered the hardness and Young's Modulus values for these coatings. AlTiN-Ni with 0% Ni content exhibited the highest values for these properties (26.2 GPa and 315 GPa for hardness and elastic modulus, respectively). These values decreased with the increase in Ni content. For a Ni content of 1.5%, the values registered for hardness and Young's Modulus were 24.3 GPa and 315.8 GPa, respectively, seeing another decrease to 20.9 GPa and 300.5 GPa for a Ni content of 3%. From these presented values, the decrease in mechanical properties was not very accentuated from 0% to 1.5% Ni content. Furthermore, the authors observed that the toughness of the AlTiN—Ni (1.5%) coating was the highest of all the coatings, improving tool life by 160%.

Still regarding the addition of elements to TiAlN-based coatings, in the study carried out by Liu et al. [62], the addition of Ruthenium (Ru) to TiAlN coatings is performed and evaluated. The authors compared the microstructures of base TiAlN coating and two other coatings with differing Ru contents—7% and 15%, respectively. As seen in the work presented above [61], it was noted that the Ru addition promoted a change in the coating's microstructure, and similar to the addition of Ni, it promoted a homogenization of the microstructure. By analyzing Figure 8, the microstructure changes from a columnar structure to a homogenous structure.

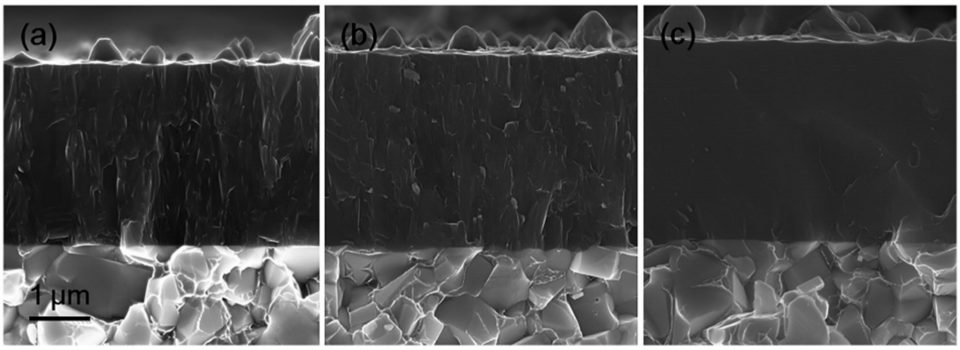

Figure 8. SEM cross-sectional image of TiAlN coatings with different Ruthenium contents: 0% (**a**), 7% (**b**), 15% (**c**), presented in the study carried out by Liu et al. [62].

An increase in mechanical properties was also registered for the coating with 7% Ru (33.15 GPa and 498.55 GPa for hardness and Young's Modulus, respectively), however, the coating with 15% Ru content showed a decrease in hardness and Young's Modulus value, even when compared to the base TiAlN coating. Other elements, such as Ytrium (Y) and Tantalum (Ta), are linked to an increase in properties for TiAlN-based coatings, as seen in the study performed by Aninat et al. [63], where the addition of Y is linked to an increase in hardness values. Ta, however, did not have a significant influence on the coating's mechanical properties, influencing the amount of residual compressive stresses of the coating, which is linked to the wear behavior of the coating. Ta coatings exhibited a better wear behavior, whereas Y doped coatings exhibited overall better mechanical properties. Regarding coating residual stress control, this factor has also been linked to coating thickness, with this being analyzed by Chandra et al. [64]. In total, three TiAlN coatings with differing thicknesses were studied. Their mechanical properties suffered low variation, exhibiting a small decrease with a thickness increase. However, the residual stresses are greatly influenced by the coating's thickness, exhibiting higher values for thinner coatings.

Another element related to a significant increase in mechanical properties is Silicon (Si), significantly increasing hardness and Young's Modulus values. TiAlSiN is an example of a TiAlN coating doped with Si. As seen in [65], TiAlSiN coatings have better mechanical properties and wear behavior when compared to TiAlN coatings.

Regarding recent improvements made on the properties and performance of TiAlN-based coatings, in the study carried out by Chaar et al. [66] two TiAlN coatings with high aluminum content and differing structures were studied. One coating had a fine-grain structure, consisting of a mixture of cubic and hexagonal phases (dual-phase coating), the other coating had a coarse-grain structure of cubic phase. It was found that, although the coatings are very similar in terms of composition, their structure greatly impacts the thermal behavior of the coatings, highlighting the advantage of controlling the coating's structure in order to obtain a desired result, especially in terms of thermal stability.

There have also been recent studies conducted on the improvement of TiAlN-based coatings' performance by applying texturing treatments to the substrates. These texturing treatments are linked with a slight increase in wear behavior and mechanical properties. Moreover, coating adhesion improves greatly in textured tools [67,68].

2.1.1. Machining Applications and Coating Wear Behavior

In this subsection the recent studies on machining applications of monolayered TiAlN-based coatings are going to be presented. An analysis of recent studies was conducted on the wear behavior of these coatings. The tool wear mechanisms suffered by monolayered TiAlN-based coatings for milling and turning are going to be presented.

Milling Process

The milling process has a huge presence in the machining industry, with many studies being conducted about the improvement of this process, either by using new tool geometries, coatings or by employing optimization techniques, such as the Taguchi method [43,69] to optimize machining parameters. TiAlN-based coatings are also being researched, in order to try and improve the various machining processes where they are employed. As seen in the beginning of this section, using doping elements to improve the coating's mechanical properties [59–64]. Other approaches to improve the performance of these coatings involve the study of coating behavior under experimental machining conditions, or the study of the wear mechanisms sustained by these coatings during machining [39,43]. Ravi et al. [70] studied the influence of various lubrication methods on TiN and TiAlN-coated tool's performance. The authors conducted milling experiments under, dry, flooded and cryogenic (liquid nitrogen) conditions. Furthermore, the tests were conducted at 75, 100 and 125 m/min of cutting speed. The cutting temperature and cutting force variation were evaluated for all tools. It was observed that the use of the TiAlN-coated tool over the TiN caused an increase in cutting performance, exhibiting a reduction of approximately 13% in cutting force for all cutting conditions. Moreover, the cutting temperature was 18% lower for the TiAlN-coated tools when compared to TiN. Cutting temperature increased with higher cutting speed values, however, cutting force values decrease for higher cutting speeds. This was particularly evident for the cryogenic cutting conditions, where the TiAlN-coated tools benefited greatly from this, exhibiting the lower cutting force value of all tools for all cutting conditions. This force variation for all coated tools under the three lubrication conditions can be observed in Figure 9.

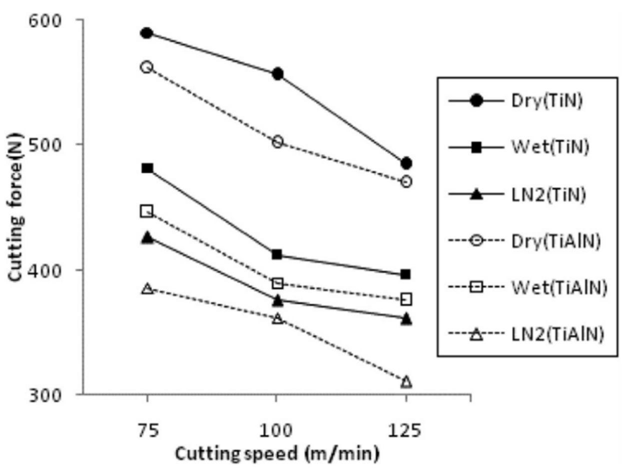

Figure 9. Cutting force variation (N) for different cutting speed values, for TiN and TiAlN-coated tools under the three different machining conditions, presented by Ravi et al. [70].

It was reported by the authors that in this case the main wear mechanism was adhesion and abrasion, for all the cutting conditions, these effects being attenuated by the employment of flooded and cryogenic cutting conditions, especially for the TiN coating. The TiN-coated tool suffered more adhesive and abrasive wear than the TiAlN-coated tool, this can be explained by the Al contained in the coating. This element can confer the coating with better thermal properties, explaining the fact that these are less affected by the temperature dependent adhesive wear. Still regarding the wear analysis of TiAlN-based coatings, Siwawut et al. [71] evaluated the cutting performance and wear characteristics of TiAlSiN and CrTiAlSiN coatings. These coatings were deposited by filtered cathodic arc onto WC (Tungsten Carbide) inserts. The authors tested the coated tools and one uncoated tool in the dry milling of cast iron turbine housings, using a range of 14–300 m/min for cutting speed. Coating's mechanical properties were evaluated, namely hardness and Young's Modulus values. The TiAlSiN coating exhibited the highest hardness value of all tools and the highest Young's Modulus value of both the coated tools, although these values have been very similar to those of the CrTiAlSiN. This produced a higher surface finish quality when using the CrTiAlSiN-coated tool when compared to the CrTiAlSiN coated tool. The H/E ratio of these coatings was also evaluated, as this ratio is strongly correlated with wear performance. The CrTiAlSiN coating exhibited the highest value of all tools (0.112), being followed by the TiAlSiN coating (0.105). The insert wear was analyzed using SEM, whose images can be observed in Figures 10 and 11.

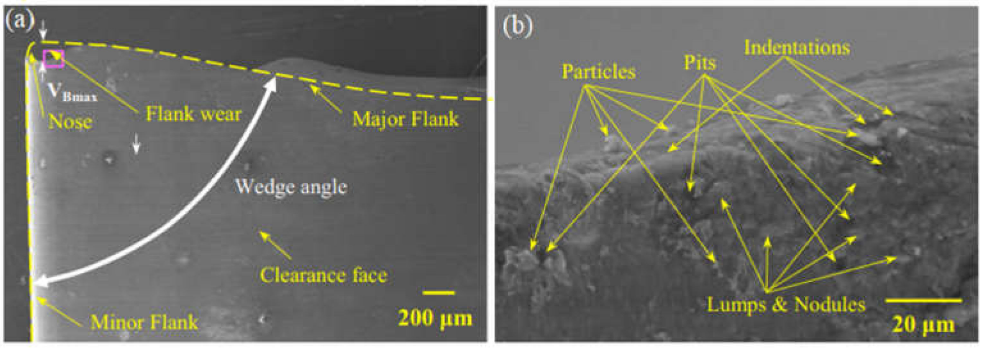

Figure 10. SEM micrographs of the TiAlSiN-coated WC insert, low magnification (**a**), and high magnification (of the zone marked with a pink square) (**b**), presented by Siwawut et al. [71].

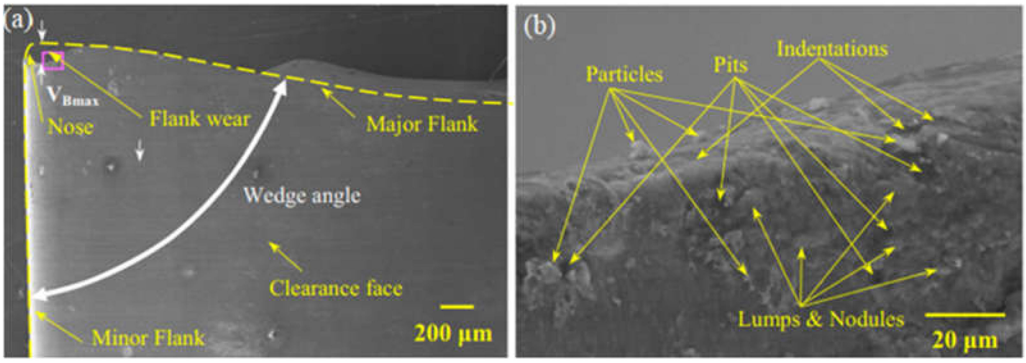

Figure 11. SEM micrographs of the CrTiAlSiN-coated WC insert, low magnification (**a**) and high magnification (of the zone marked with a pink square) (**b**), presented by Siwawut et al. [71].

Both the coatings improved the wear behavior of the WC inserts, however, the CrTiAlSiN coating performed better in this regard, exhibiting lower values for flank wear and suffering overall less damage, when compared to the TiAlSiN-coated insert. The authors observed that TiAlSiN-coated inserts displayed primarily ploughing abrasive wear behavior, while the CrTiAlSiN-coated inserts exhibited wear related to thermal cracking and partial coating delamination.

As mentioned previously, the level of residual stresses inside the coatings impacts their properties and, thus, their machining performance [30,38,39,43]. There are some recent studies made on this topic, as the work presented by Hou et al. [72], where the influence of compressive stresses on the TiAlN-coated tool's performance when milling Ti alloy Ti-6Al-4V was investigated. Both coatings had the same composition and were deposited onto the same substrate material, one of them was unaffected by compressive stresses (Coating 1) and the other was affected (Coating 2). These coatings were characterized, determining hardness and Young's Modulus values, presented in Table 2.

Table 2. Hardness and Young's Modulus values determined for TiAlN coatings (Coating 1 and 2), presented by Hoy et al. [72].

Coating	Hardness (GPa)	Young's Modulus (GPa)
1 (Unaffected)	30.6	482
2 (Affected)	34.9	567

The residual stresses have a clear benefit for the coating's mechanical properties, with Coating 2 having an increase in hardness and Young's Modulus values by 12% and 15%, respectively. These were then subjected to milling tests, having their wear behavior analyzed. In Figures 12 and 13 the wear mechanisms sustained by the two coated tools can be observed.

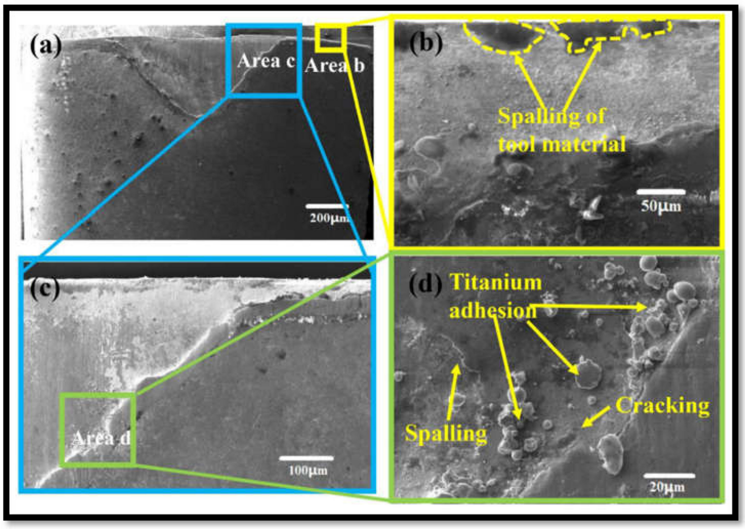

Figure 12. Wear patterns exhibited by Coating 1 after machining: SEM image of flank face (**a**); magnification of area b (**b**); magnification of area c (**c**); magnification of area d (**d**). Presented by Hou et al. [72].

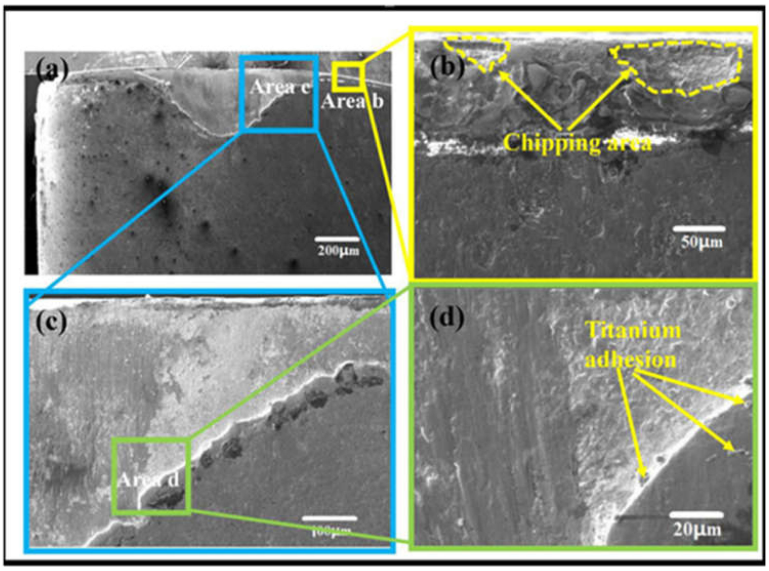

Figure 13. Wear patterns exhibited by Coating 2 after machining: SEM image of flank face (**a**); magnification of area b (**b**); magnification of area c (**c**); magnification of area d (**d**). Presented by Hou et al. [72].

From Figures 12 and 13, it can be observed that the wear sustained by Coating 1 is more intense than that of Coating 2, the former presenting more cracking and spalling than the other coating. There is, however, material (titanium) adhesion on both the tool coatings. The sustained flank wear over the cutting length for both coatings was also analyzed. The authors determined that the wear was less intense on Coating 2. The wear behavior for both coatings can be observed in Figure 14.

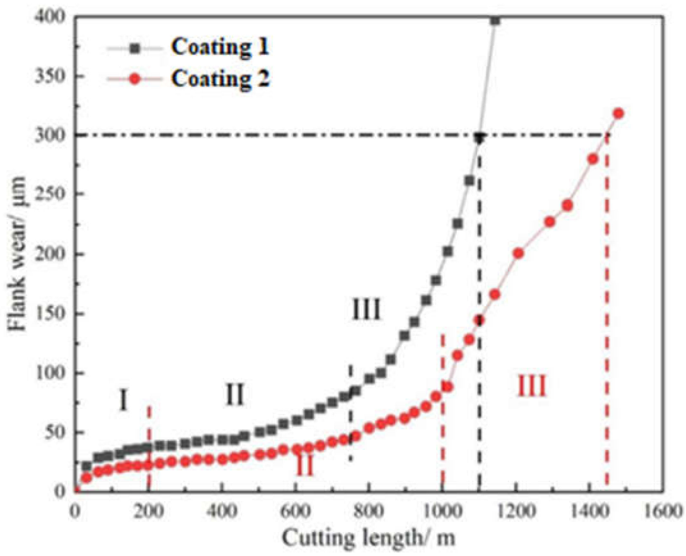

Figure 14. Flank wear measurements (μm) for various cutting lengths, for both coatings, presented by Hou et al. [72].

Compressive stresses can improve the wear behavior greatly and reduce the wear, as seen from Figures 12 and 13, because the coating unaffected by stresses suffered more cracking, and subsequently, coating spalling damage, while the coating affected by compressive stresses exhibited less cracking and less wear damage for equal cutting length values. As the crack propagates deeper into the coating, high stress values can prevent this crack propagation, retarding this damage.

As seen from presented recent works, there seems to be a focus on the optimization/study of milling processes of hard-to-machine materials, as titanium alloys [72] and some other alloys with high strength applied primarily to the aeronautical industry such as aluminum, particularly from the 6000 and 7000 series [69]. Another of these alloys is Inconel, with some recent works being conducted on the study of milling cases of this alloy. TiAlN coatings have seen some application in the machining of this alloy, as seen in the study performed by Sen et al. [73], in which the wear behavior of TiAlN coated carbide tools is analyzed in the milling of Inconel 690. Similar to the study presented by Ravi et al. [70], the authors have studied the influence of different lubricating conditions on the performance of TiAlN coating, using flooding, MQL (Minimum Quantity Lubricant) with palm oil, and MQL with 0.9% alumina enriched palm oil. Due to the high temperatures developed during the machining of this material and its characteristic high hardness, the wear mechanisms that were reported were mainly abrasion and adhesion. The wear related to these mechanisms can be observed in Figure 15. This was registered for all the lubricating conditions, however, the MQL 0.9% alumina enriched condition led to less wear damage on the tool.

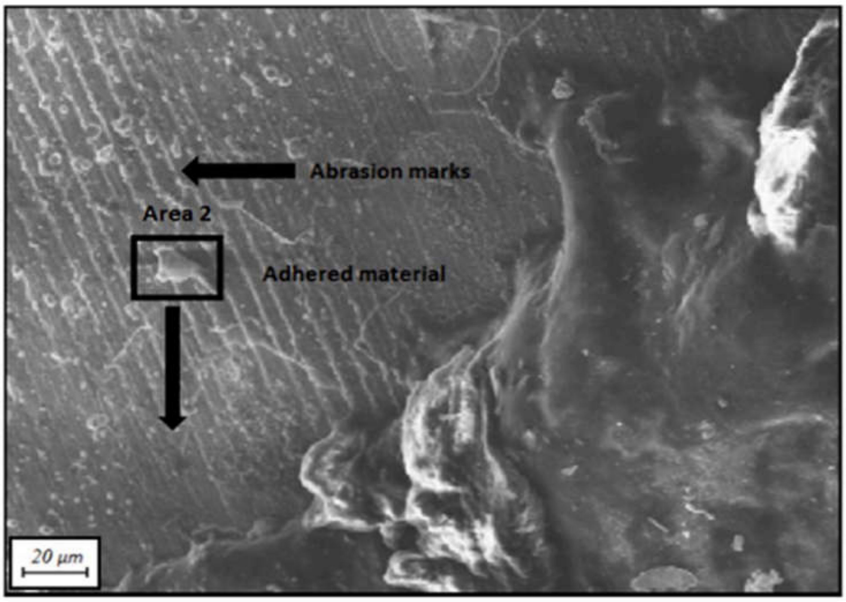

Figure 15. Abrasion marks and adhered material on TiAlN coating after milling of Inconel 690 (under the MQL with palm oil lubricating condition), presented by Sen et al. [73].

The main wear mechanisms that TiAlN-based coatings suffer in milling operations are mainly adhesion and abrasion. These mechanisms are more evident and intense in the milling experiments conducted on hard-to-machine materials, where the high machining temperature and material hardness heavily impacts tools life. High hardness values will induce heavy abrasive wear on the coatings and the high temperatures will promote adhesion of the machined material to the tool. This leads to coating delamination and, ultimately, to tool failure. These wear mechanisms are also registered for micro-milling experiments. There is a recent trend for the application of TiAlN based coatings for micro-milling [74], this because of the properties that make this coating ideal for high-speed machining, whose are also suited for this process, due to high rotational speeds usually used in micro-machining. Recent studies focus on the machining of hard-to-machine alloys [75], employing TiAlN coatings and AlTiN [76] coatings in the machining of titanium alloys [75,76] and nickel-based superalloys, such as Nimonic 75 [77]. The main wear mechanism sustained by coated micro-milling tools, when machining hard-to-machine materials, are adhesion and abrasion, as seen for the milling process, with cutting speed and depth of cut being registered as the main influencer on the development of this wear.

Turning Process

The turning process as also seen some applications of monolayered TiAlN-based coated tools. Studies made on this topic, similarly to the ones conducted on the milling process, evaluate various coatings performances and wear behavior. The studies seem to focus on the turning of hard-to-machine alloys, however, these are focused primarily on the machining of Inconel. Zhao et al. [78] study the influence of coating thickness on the machining performance of TiAlN-coated tools. The authors studied two TiAlN coatings, TiAlN-1 having 1 μm thickness, and TiAlN-2 with 2 μm thickness. Both coatings were deposited onto a WC-Co carbide and were employed in the dry turning of Inconel 718. Turning tests were performed at the cutting speeds of 30, 60, 90 and 120 m/min. The cutting forces developed during turning were evaluated, concluding that using coating with less thickness would result in lower cutting force values. Moreover, the cutting temperature was lower when using the thinner coating. Regarding the wear mechanisms and wear behavior of these coatings, these are presented in Figures 16 and 17. These images depict the wear sustained by both coatings at the tested machining speeds.

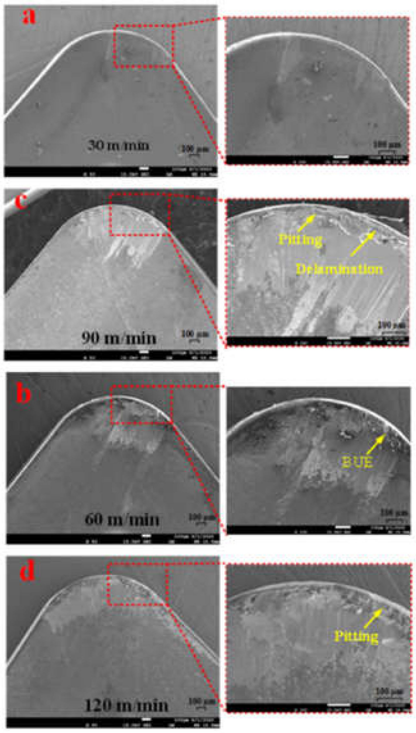

Figure 16. Wear of TiAlN-1 coated tool at different cutting speeds: 30 m/min, with magnification of marked area (**a**); 60 m/min, with magnification of marked area (**b**); 90 m/min, with magnification of marked area (**c**); 120 m/min, with magnification of marked area (**d**), presented by Zhao et al. [78].

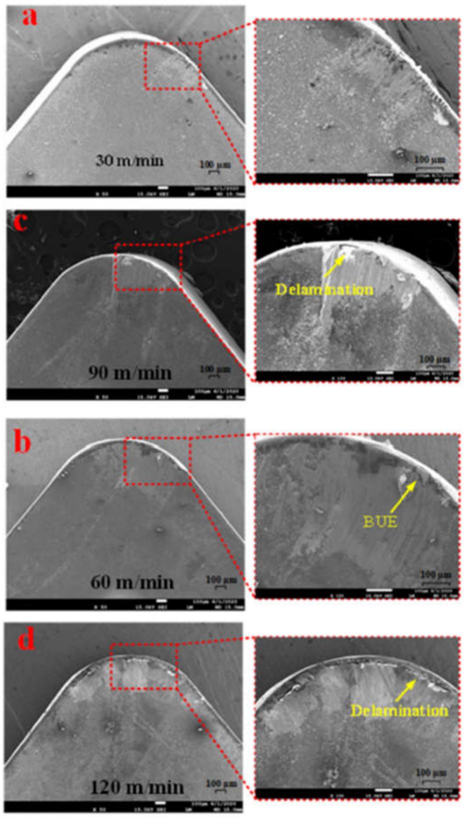

Figure 17. Wear of TiAlN-2-coated tool at different cutting speeds: 30 m/min, with magnification of marked area (**a**); 60 m/min, with magnification of marked area (**b**); 90 m/min, with magnification of marked area (**c**); 120 m/min, with magnification of marked area (**d**), presented by Zhao et al. [78].

The presented coatings both exhibit the same type of wear mechanisms, these being built-up edge (BUE), pitting and coating delamination. From the figures it can be noted that adhesion is also a problem, this last mechanism being responsible for BUE and coating delamination. These wear mechanisms, as in milling, are characteristic of machining hard-to-machine materials such as Inconel, due to material's mechanical properties. Still regarding TiAlN coating's performance when turning Inconel, the study performed by Kurniawan et al. [79] evaluates the machinability of modified Inconel 713C, using a TiAlN-coated WC tool. The cutting characteristics of Inconel 713C are very similar to those of Inconel 718, making it a very hard to machine material. The authors have reported abrasive wear as the main wear mechanism in the tool's flank, being followed either by tool failure or BUE (Build up Edge) formation, as can be observed in Figure 18. High machining temperatures and the ductility of Inconel 713C, caused material adhesion to the tool, which promoted abrasive wear and subsequent coating delamination.

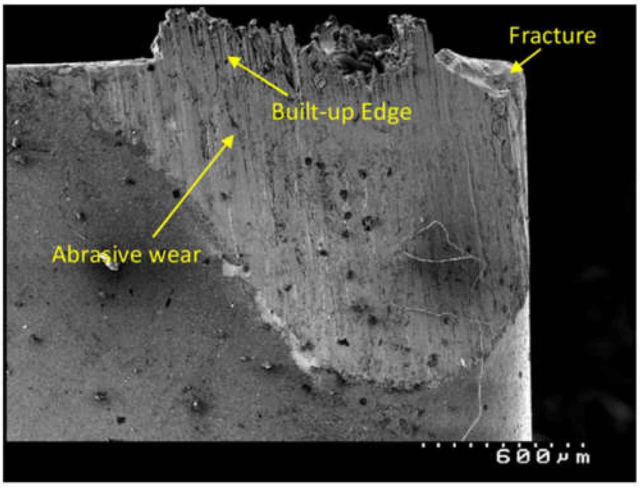

Figure 18. Flank wear of TiAlN-coated WC turning tool at 100 m of cutting distance used in machining Inconel 713C, presented by Kurniawan et al. [79].

Another study performed by Zhao et al. [80], studies the cutting behavior of AlTiN coatings on the turning of Inconel 718 at cutting speeds of 40, 80 and 120 m/min. Machining temperature and cutting forces were evaluated and compared to an uncoated tool. These factors both decreased when using the AlTiN coated tool, proving that this coating is suited for the turning of these alloys. Similar to the studies presented in [78,79], the main wear mechanism suffered by the tools during machining was abrasive wear. Both the TiAlN and AlTiN coatings proved to be very useful when machining hard-to-machine materials, effectively reducing cutting force and machining temperature values. These values are tied to wear rate, with the coated tools exhibiting a significantly lower wear rate than uncoated turning tools [81]. The addition of Si to TiAlN coatings is known to significantly improve their mechanical properties [71], thus making these types of coatings ideal for the machining of materials such as titanium alloys. Lu et al. [82] compares the performance of TiAlN and TiAlSiN-coated tools in the high-speed turning of TC4 titanium alloy. The authors also studied the performance of a gradient TiAlSiN coating. The microstructures of these coatings and the distribution of Si on the gradient coating can be observed in Figures 19 and 20.

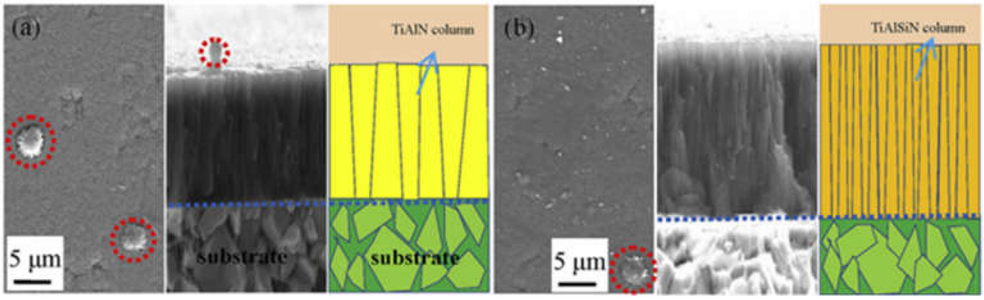

Figure 19. Surface morphology and microstructure of: TiAlN coating (**a**); TiAlSiN coating (**b**), presented by Lu et al. [82].

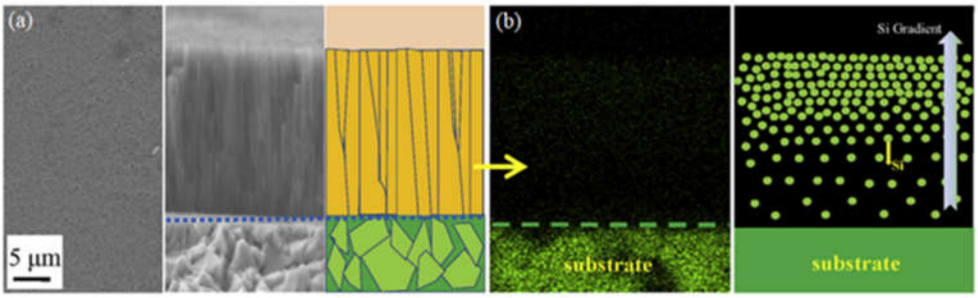

Figure 20. Surface morphology and microstructure (**a**), and Si distribution on TiAlSiN gradient coating (**b**), presented by Lu et al. [82].

The coating's hardness was also evaluated, the TiAlSiN coating exhibiting the highest hardness value (21 GPa) followed by the gradient TiAlSiN coating (15 GPa). The gradient TiAlSiN coating presented an increase in hardness by 47% when compared to the TiAlN coating. An improvement in surface quality and adhesion is also registered for the gradient TiAlSiN coating. All the machining experiments were conducted at 100 m/min cutting speed under flooded lubrication. The coated tools exhibited the same wear mechanism, this being mainly abrasion and BUE, with some adhesion being registered on the TiAlN coated tool. Although the wear mechanism has been the same, their intensity varied, being more intense in the TiAlN coated tool. The coated tool's wear behavior is depicted in Figure 21, where flank wear values (measured in mm) are displayed for the three coatings, for various cutting lengths.

The improved adhesion and surface quality of the gradient TiAlSiN, coupled with the increase in mechanical properties due to the addition of Si provides this gradient coating with great wear performance, suffering overall less wear and at a much later stage in the machining process. Still regarding the addition of elements to improve coating turning performance, in the study performed by Kulkarni et al. [83] the authors study the influence of Cr addition to AlTiN coatings. Here, the authors evaluate the turning performance of AlTiN, AlTiCrN and TiN/TiAlN coated tools, by analyzing cutting forces, wear mechanism and tool-life values. The coating's microstructure was evaluated, with all coatings showing a dense columnar structure, however, in terms of surface morphology, the AlTiCrN coating exhibited a smooth surface. Furthermore, the adhesion strength of this coating was the highest of all three. The coatings were employed in the dry turning of SS 304 steel at a constant feed rate and depth of cut, varying the cutting speed from 140 to 320 m/min (in 60 m/min increments). Regarding the cutting force values registered during the process, these tended to decrease as cutting speed increases, however, the AlTiCrN coating exhibited the lowest cutting force values obtained of all coatings. This can be observed in Figure 22.

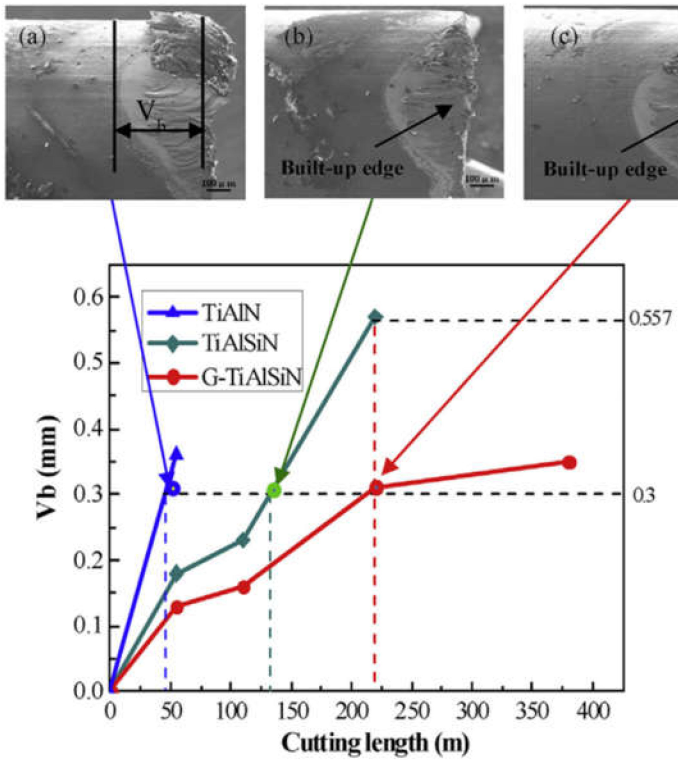

Figure 21. Tool wear of the three coated tools tested in the turning of TC4 titanium alloy: TiAlN (**a**), TiAlSiN (**b**), Gradient TiAlSiN (**c**), presented by Lu et al. [82].

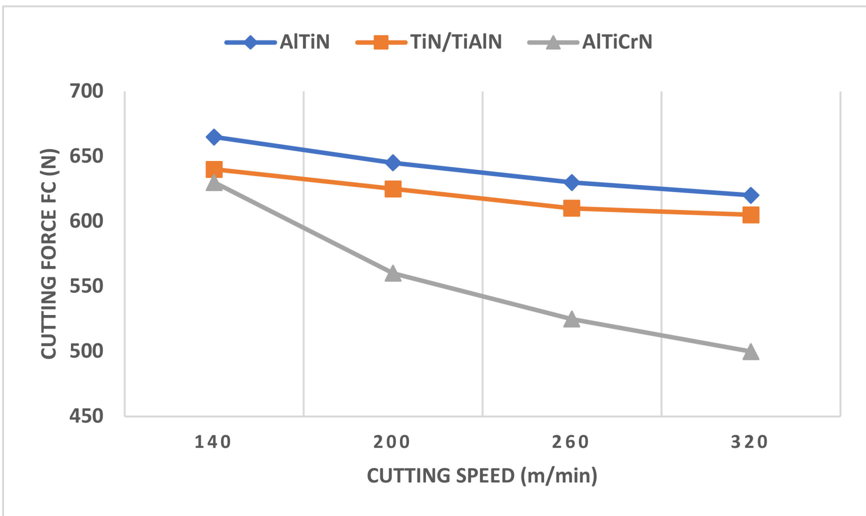

Figure 22. Cutting force variation for the tested cutting speeds, for all coated tools at the following parameters: depth of cut = 1 mm; feed = 0.2 mm/revolution (based on data from [83]).

For the AlTiN tool, the main wear mechanisms were abrasion, chipping and BUE. This was registered for the TiN/TiAlN coating as well, however, there was some adhesive wear. For the AlTiNCrN coating, the main wear mechanism was abrasion, albeit less intense than in the AlTiN coating. Regarding tool-life of these coated tools, it tended to decrease with an increase in cutting speed. Further, as seen for the cutting forces, the AlTiCrN coating outperformed the other coated tools, exhibiting the highest tool life values, reaching 28 min (at 200 m/min). These values can be attributed to the coating's excellent adhesion properties, smooth surface and having high hardness.

From the presented articles conducted about the turning process using TiAlN-based tools, it can be concluded that the main wear mechanisms that coated turning tools are subjected to are, abrasion and adhesion, with the formation of BUE [39]. In the following Figure 23 a clear example of BUE can be observed; in the image the built up material can be seen the coated tool's edge.

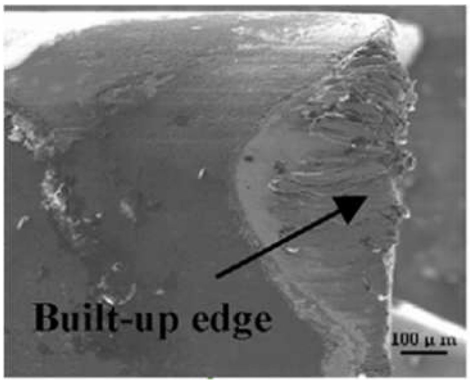

Figure 23. BUE observed at a gradient TiAlSiN-coated tool's tip, after some machining (roughly 125 m of cutting length [82].

2.1.2. Comparison of the Coating's Mechanical Properties

In this chapter an analysis of the mechanical properties of the monolayered TiAlN-based coatings registered in the various works presented in this section is going to be presented. The best hardness and Young's Modulus values for the main coatings, that were obtained by the various authors, were collected, and are presented in Table 3.

Table 3. Monolayered TiAlN-based coatings mechanical properties.

Coating	Hardness (GPa)	Young's Modulus (GPa)
TiAlN [60,64–66,68,84–86]	29.2–34.9	482–511
AlTiN [67,85]	20.0–24.3	337–358
TiAlSiN [65]	25.2–29.8	266–288
CrTiAlSiN [71]	24.0–27.1	200–275
AlTiN–Ni [61]	20.9–24.3	300–316
TiAlMoN [59]	21.58–37.0	510–620
TiAlYN [63]	31.6–35.2	520–575
TiAlTaN [63]	27.0–31.0	542–588
TiAlTaYN [63]	31.7–34.3	526–568
TiAlRuN [62,87]	26.09–33.2	334–492

The addition of elements is a very influential factor on the coating's mechanical properties. However, the coating's deposition method, microstructure and level of residual stresses also impact on the coatings' mechanical properties, with some elements having a greater influence on the hardness, such as Si and Cr. This hardness increase is well documented for these elements, with coatings such as TiAlSiN seeing great use in machining applications, due to its increased wear performance when compared to base TiAlN coatings. New doping elements are being tried, with good results coming from the addition of elements such as Mo, Ru and Y, causing a significant increase in hardness and Young's Modulus values. However, research regarding machining applications for TiAlN-based coatings doped with these elements is quite sparce, as these types of coatings are quite novel. The addition of Ta is also quite novel for monolayered, yet this element was already implemented in the architectures of multilayered TiAlN-based coatings.

Some deposition methods and even variations on the composition of TiAlN-based coatings, such as TiAlN and AlTiN, also influence their mechanical properties (as seen in Chapter 1). One common case study is the evaluation of the coating's residual stresses on their mechanical properties and wear behavior. In most cases, some amount of residual compressive stresses is preferred, as it usually increases hardness and Young's Modulus values. Furthermore, these stresses are also related with better wear performance, lowering coating wear rates and crack propagation.

Regarding these coatings wear behavior, from the works presented above, it can be noted that the H/E ratio heavily influences the coating's wear performance, with a higher value being usually preferred. This ratio is presented in Figure 24, based on the information provided by Table 3. From the analysis of the table, it can be noted that CrTiAlSiN and TiAlSiN coatings are the ones with the highest H/E value. This is especially due to the addition of elements such as Cr and Si, that confer the tool with excellent mechanical properties and wear behavior. The TiAlMoN coatings also show a high ratio value, making them a very promising coating for machining applications. Furthermore, the addition of Mo also promotes a better corrosion resistance of the coated tool. Although these values can be indicative of the coating's wear performance, this is also dependent on the machined material. For example, coatings with low hardness value will experience more abrasion (despite having a higher H/E ratio). Thermal fatigue is also a factor, for example, while the CrTiAlSiN coating is less susceptive to the wear mechanisms such as adhesion and abrasion, which revealed has suffered from thermal cracking due to the machining's high temperatures [71]. This highlights the fact that coating choice is very important for a certain machining operation.

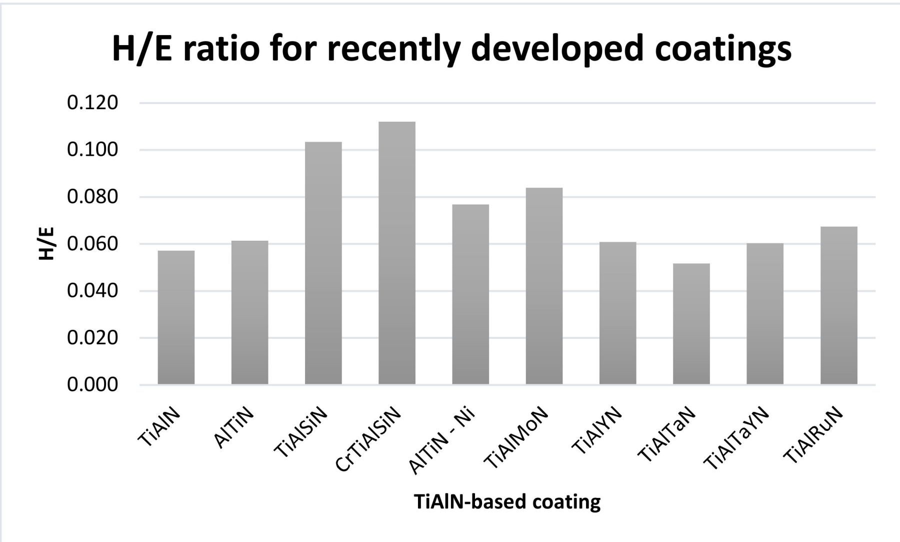

Figure 24. H/E ratios for the analyzed monolayered TiAlN-based coatings.

It is also worth to note that, although some coatings have very similar H/E ratios, their composition influences greatly their wear behavior and it should be factored on the coating choice.

2.2. *Multilayered TiAlN-Based Coatings*

Multilayered coatings are very appealing to the machining industry, as they enable combinations of various coating's properties to best fit a machining application. Further, their multilayered structure prevents crack growth [23,53]. This versatility makes them the most used type of coatings, in terms of coating structure, in the machining industry, for both the turning and milling sectors [39,43]. In terms of multilayer coating developments in general, there seems to be a trend in optimizing layer thickness [39]. Furthermore, there is a focus on studying the behavior of various types of coating combinations. This seems to be the case on the studies conducted around TiAlN-based coatings. Analyzing recent studies made on this regard, new combinations based on the coatings presented in Section 2.1 are being studied. There are also some studies about the improvement of already well-known TiAlN-based multilayered coatings, such as the TiAlN/TiN, Ti/TiAlN and TiN/TiAlN coatings, as seen in this work conducted by Zhang et al. [88], where the authors study the cyclic oxidation of Ti/TiAlN coatings with differing thicknesses of Ti layer, having 0.15 and 0.3 μm for coating 1 and 2, respectively. TiAlN single layer coatings with differing thicknesses were also studied. Regarding the results obtained for the multilayered coatings, it was noted that the residual stresses of the thinner coating would be relieved after the tests. This coating exhibited cracking, as the stresses could not be accommodated. However, for the coating with the thicker Ti layer, the residual compressive stresses increased, with this coating showing no cracking due to the thicker ductile Ti layers. This is a relevant study, as compressive stresses contribute for the tribo-mechanical properties of the coating, leading to a better cutting performance [89]. Regarding the study of TiAlN/TiN coatings, Çomakli [90] compares the mechanical and corrosion properties of TiN, TiAlN and multilayered TiAlN/TiN-coated tools. It was reported that the multilayered coating presented a smoother surface, having a smaller grain than the surfaces of the other coatings. The hardness for the multilayer coating was also higher, due to the number of layers present in the coating [39,43]. Due to the combination of coating surface and mechanical properties, the multilayered coating had a lower friction coefficient, conducing to a lower wear rate. A similar study employs the use of CrN (Chromium Nitride) on a multilayered architecture for TiAlN coatings [91]. The author compares the wear performance and mechanical properties to TiAlN monolayer coating, reaching similar conclusions to those of the previous study, significantly improving the wear behavior by reducing the friction coefficient, while increasing the coating's mechanical properties.

As mentioned in the study presented above [88], the addition of interlayers of Ti can improve the wear performance of multilayered coatings. Similar to this, the work completed by Shugurov et al. [92] studies the influence of TiAl interlayers on a TiAlN-based multilayer coating. The authors study the influence of the number of layers/interlayers and their respective thickness on coating's mechanical properties and their wear behavior. The coating's structure can be observed in Figure 25.

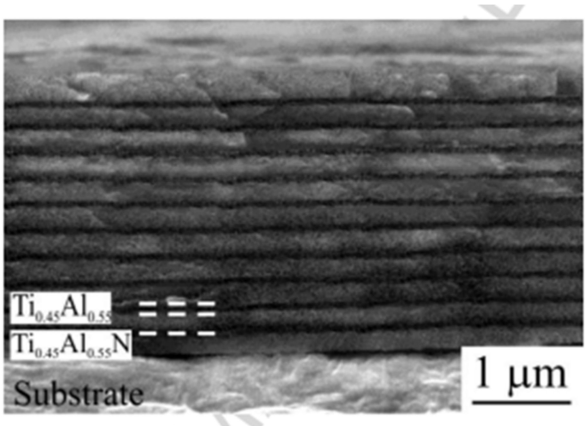

Figure 25. Multilayer structure of one of the TiAlN/TiAl coatings presented by Shugurov et al. [92].

The authors concluded that four layers of TiAlN and three interlayers of TiAl with thicknesses of 0.6 and 0.2 μm, respectively, would produce the best wear performance, exhibiting a wear rate three times inferior to that of the monolithic TiAlN coating. The results of this study provide very useful information regarding coating design, as this method can be used for a wide range of applications, especially machining.

The use of Ta is also being recently researched, as shown in the work presented in Section 1 [27], where various multilayered TiAlTaN-(TiAlN/TaN) with differing layer thicknesses were tested and subsequently characterized. In another recent study carried out by Shang et al. [93], the mechanical properties of a multilayered TiAlN/Ta coating are evaluated. The coating consists of three layers, a TiAl layer followed by a TiAlN layer and finally, a Ta layer (Figure 26). The mechanical properties of the multilayered coating were compared to a TiAlN monolithic coating. TiAlN/Ta coating exhibited a higher value of hardness and elastic modulus (31 GPa and 315 GPa, respectively), showing an increase of 29% and 47%, respectively. Ta is a ductile material and can dissipate energy through deformation, thus minimizing crack propagation. Furthermore, this element confers the coating with a better thermal stability. Studies such as these [27,93] show that Ta is very beneficial to improve TiAlN-based coating's wear behavior.

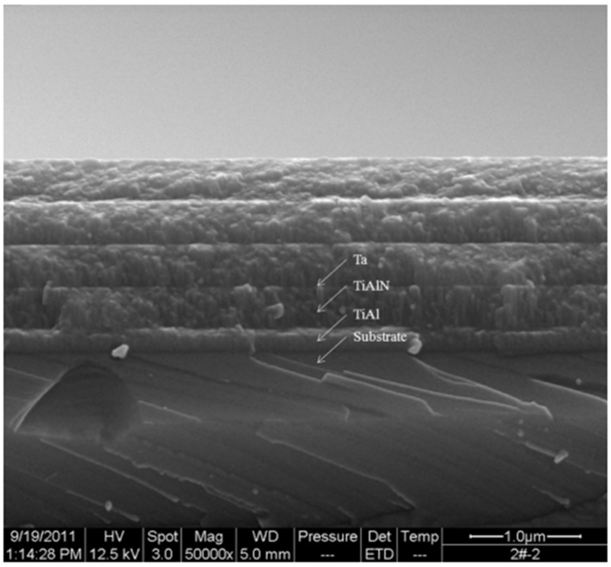

Figure 26. SEM cross-sectional image of the TiAlN/Ta multilayered coating, presented by Shang et al. [93].

It is known that multilayered coatings benefit from all the properties of their layers, as seen in the previous study [93], where a Ta layer promoted a lower wear rate for the coating, based on its ductility (primarily). This can be true for the same coating, yet with different mechanical properties, as seen in this study performed by Zhao et al. [94], where various multilayered TiAlSiN coatings are studied. These coatings consist of alternating layers of TiAlSiN deposited at different chamber pressures, thus causing hardness variation between the two coatings. TiAlSiN-1, obtained at 0.08 Pa chamber pressure presented 32.25 GPa of hardness, while the TiAlSiN-2, obtained at 0.2 Pa, exhibited 37.56 GPa for hardness value. Coatings were produced with 2, 5, 7 and 10 alternating layers of TiAlSiN-1 and TiAlSiN-2. It was observed that the hardness values for coatings with five or more layers were very close (of about 37 GPa). This was also the case for their elasticity modulus, however, the coating with five alternating layers showed the best plastic deformation resistance, and thus, the lowest wear rate. Though, the wear rate for coatings with five or more layers were very similar. The wear behavior of the multilayered coatings was also compared to monolayered TiAlSiN coatings, the former being significantly lower than the latter. There are also some recent coatings being developed, showing promising results, such as the TiAlCN/TiAlN coatings [30], and the TiCrAlCN/TiAlN [95]. These coatings show promising results in terms of hardness and wear behavior, however, the amount of research made around them is still quite sparse.

Although the multilayered coating is the most used in machining, recent study trends show that most of the research made about these types of coatings is about nano-multilayered coatings. This is justified by the ability to obtain very thin layers using recent technologies. These types of coatings will be the focus in Section 2.3.

In the next section, recent machining applications of the TiAlN-based multilayered coatings are going to be presented. This will be done in the same manner as in the previous Section 2.1.1.

2.2.1. Machining Applications and Coating Wear Behavior

Recent machining applications for TiAlN-based coatings were analyzed. As for the development and study of multilayered coatings, recent machining applications tend to be centered on nanolayered and nanocomposite coatings. However, there is still some research being made about the use of regular multilayered coatings in machining operations, namely milling in turning.

Milling Process

Regarding the study of the wear behavior of multilayered coated tools, there has also been some research made on this regard. Based on its versatility, the multilayered coating is very popular in the machining industry. However, in terms of recent research, there are few papers made on the study of the milling performance of new TiAlN-based multilayered coatings.

Due to their versatility and multilayer structure, these types of coatings usually outperform regular monolayered coatings, especially due to their toughness and crack propagation resistance. With recent studies such as the one developed by An et al. [96], where the performance of CVD and PVD coatings on the face milling of Ti-6242S and Ti-555 titanium alloys is evaluated. The PVD coatings is a multilayered TiAlN+TiN coating and the CVD coating is a TiCN+Al_2O_3+TiN coating. The cutting forces were evaluated and during the process, these were lower for the use of the PVD coating, as seen in Figure 27.

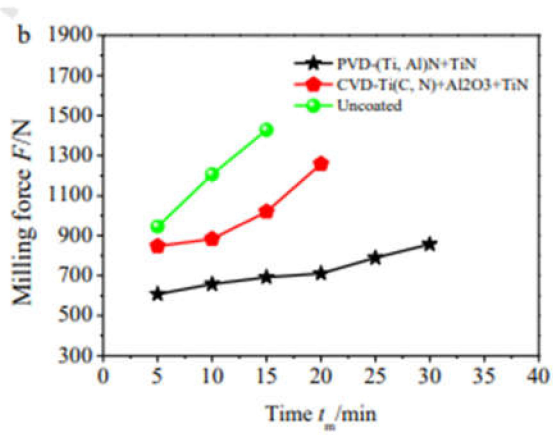

Figure 27. Cutting force value over machining time, for uncoated, PVD and chemical vapor deposition (CVD)-coated tools, presented by An et al. [96].

The wear sustained by the coated tools was also evaluated, reporting for the milling of Ti-624S that the main wear mechanisms for both CVD and PVD coating was micro-chipping and adhesive wear. Milling tests carried out on the Ti-555 alloy produced severe chipping and adhesive wear on the CVD-coated tool. However, in the PVD-coated tool, the main wear mechanism was adhesion, being less severe than with the other tool. The TiAlN-based coating proved to be better suited for the milling of these titanium alloys, showing better wear resistance and fracture resistance than the CVD-coated tool (the wear sustained by the PVD tools can be observed in Figures 28 and 29). This is not only due to the TiAlN properties for high-speed machining, but also due to the multilayered structure and residual stresses, characteristic of PVD coatings [43]. These characteristics make these types of coating highly resistance to crack propagation. Still regarding TiAlN-based multilayer coating applications in milling processes, the TiAlN/NbN coating is also known for its machining applications, due to their excellent mechanical properties, as shown by Varghese et al. [97], where they determine the coating's properties and employ them in the dry end milling of AISI 304 steel. The authors studied and evaluated the wear suffered by the coated inserts, reporting that abrasion was the main wear mechanism, eventually resulting in coating chipping and breakage.

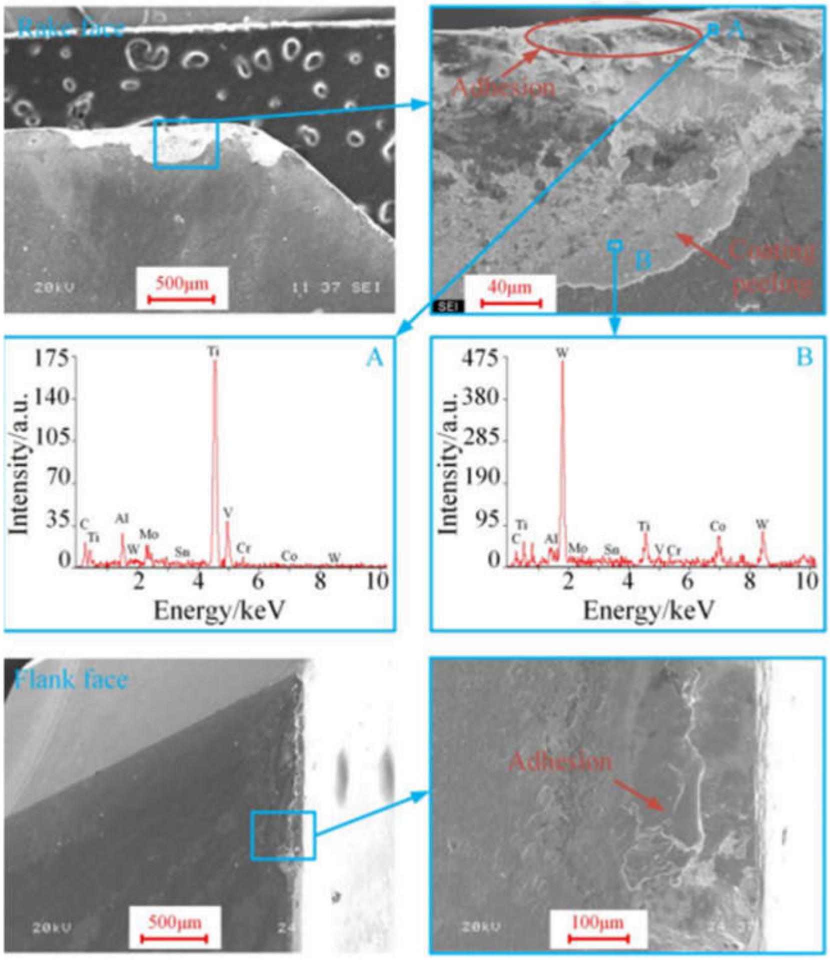

Figure 28. SEM and EDS analysis of the PVD coated tool's wear in milling Ti-555, EDS graphics correspond to the zones A and B, providing information regarding element composition, presented by An et al. [96].

As seen from Figures 28 and 29, and the results reported by the authors, the wear mechanisms sustained by multilayered coated tools in milling are very similar to those sustained by monolayered coated tools. Indeed, the main wear mechanisms present in the milling process are adhesion and abrasion. However, the multilayer architecture contributes to an improvement of coating's properties, such as wear resistance and crack propagation resistance. This causes these mechanisms to manifest at a much later stage of the machining process, albeit, in a similar way to monolayered coatings.

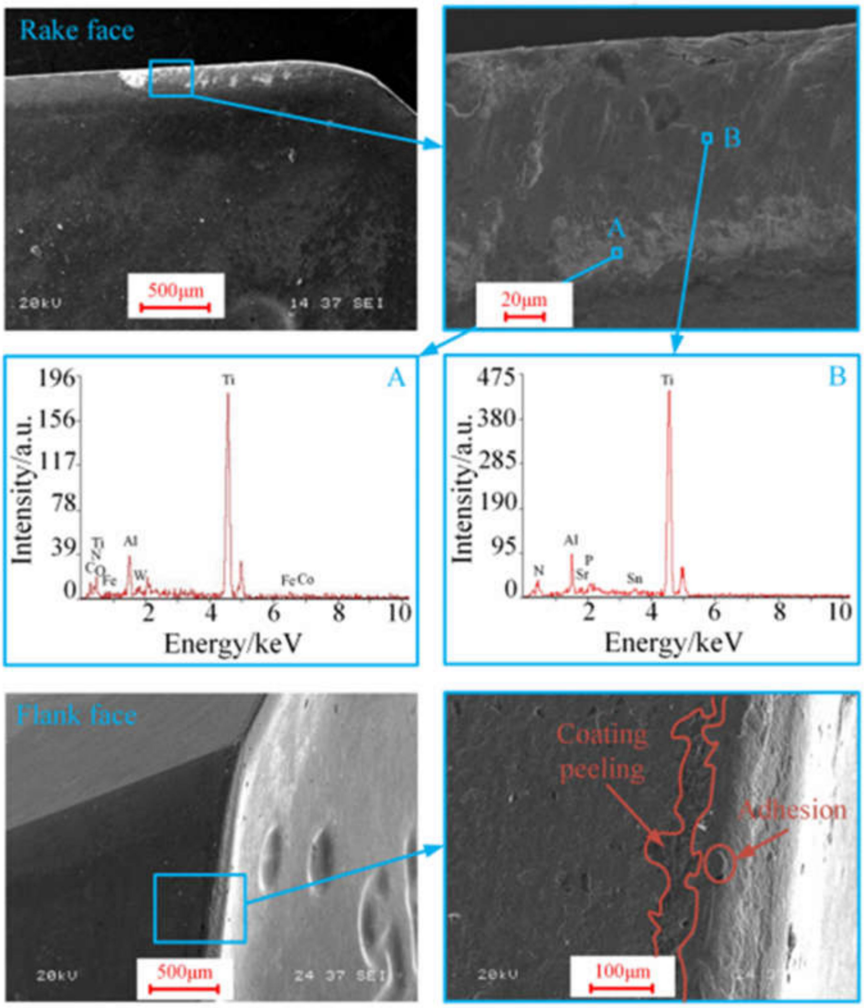

Figure 29. SEM and EDS analysis of the PVD-coated tool's wear in milling Ti-624S, EDS graphics correspond to the zones A and B, providing information regarding element composition, presented by An et al. [96].

Turning Process

Similar to the case of multilayered TiAlN-based coatings for milling applications, there seems to be very few new researches being made on this topic, with the attention being shifted to nanolayered and nanostructured coatings. However, there are some recent studies that focus on the wear performance of well-known TiAlN-based multilayered coatings, such as TiAlN/TiN. Analyzing their wear mechanisms when machining certain materials, such as in the study presented by Zheng et al. [98], in which the wear mechanisms of TiAlN/TiN coated tool are analyzed, for dry turning of 300 M steel. The coated tool suffered was mainly mechanical abrasion and adhesion, leading to chipping and coating delamination. It was also reported the existence of micro-cracks in the tool flank. This is due to the high machining temperatures developed during dry turning, which also promoted adhesion. The TiAlN/TiN-coated tool's wear can be observed in Figure 30.

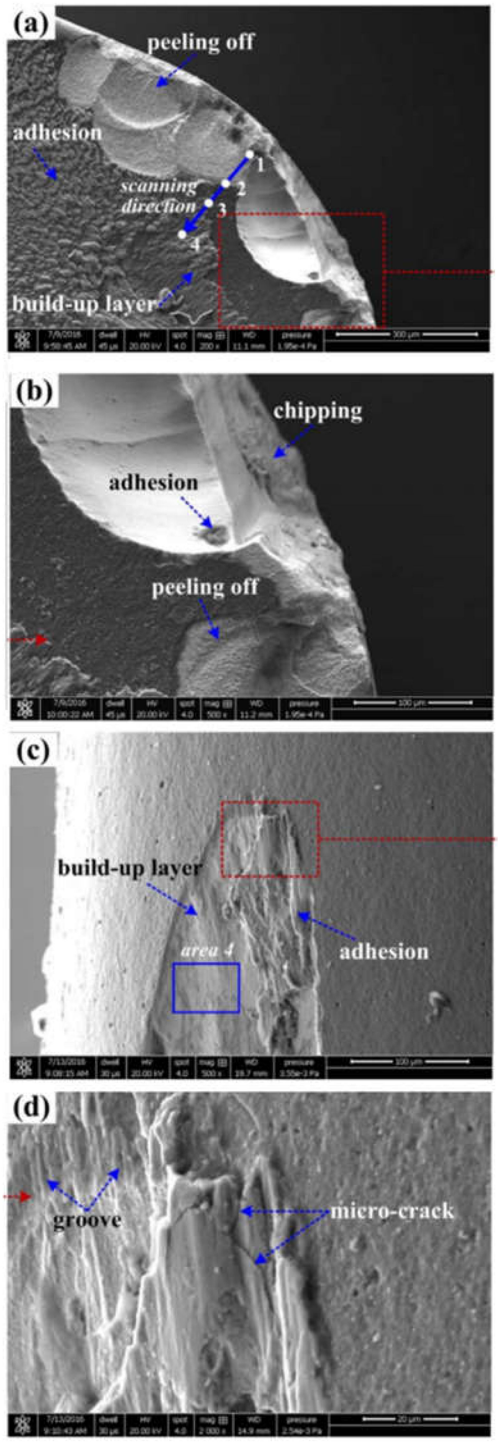

Figure 30. TiAlN/TiN-coated tool wear after dry turning of 300 M steel, rake face with 200× magnification (**a**) and 500× (**b**) and flank face with 200× magnification (**c**) and 500× magnification (**d**) presented by Zheng et al. [98].

The use of these types of multilayer coatings in hard-to-machine materials, and the study of its wear mechanisms is still a relevant subject. As the use coatings reduces machining forces and wear rates, thus making the dry machining method viable for the machining of these alloys. The use of TiN/TiAlN coating in the dry turning of Inconel 825 is studied by Thakur et al. [99], for finishing and roughing conditions. In total, three lubrication techniques were employed; these being dry, flooded and MQL. However, only the coated tool was employed in the dry machining. For the coated tool, the machining forces that were registered were lower, the surface finish of the machined material was better. However, the machining temperature was the highest for coated tool use. Wear was also analyzed for the tested tools, registering main wear mechanisms as abrasion and BUE and some minor coating delamination for the TiN/TiAlN-coated tool.

Multilayered TiAlN coatings are also being studied for turning applications. It is known that compressive residual stresses can improve cutting behavior and wear behavior of the coated tool's, however, to much compressive stresses can be detrimental for the coating's properties. As seen in this paper by Abdoas et al. [100], where the authors deposit three 11 μm thick TiAlN multilayer coating with different levels of residual stress. The three coatings, having 1.3 GPa, 2.1 GPa and 4.5 GPa, showed different cutting performances, with the coatings with fewer residual stresses having the most tool life. However, in terms of surface roughness, these coatings produced very similar results. The increase in tool life for the coating will less stresses, can be explained by the fact that this coating had better adhesion properties than the other coatings, thus promoting a better wear behavior for the coated tool. As for the wear mechanisms, these were the same for all three coatings, albeit in different intensities. The main ones that were registered were: material adhesion and BUE, with some abrasion being registered as well. This follows a similar trend to the wear mechanisms registered in monolayered coatings, similar to the milling cases mentioned in this section.

2.2.2. Comparison of the Coating's Mechanical Properties

As in Section 2.1.2, here the mechanical properties of the studied multilayered TiAlN-based coatings are going to be presented. These values are taken based on the results presented in various articles about the development/study of these types of coatings. Unfortunately, the table is missing some values that were not provided by the authors.

The various multilayered coating's properties are now going to be presented in Table 4.

Table 4. Multilayered TiAlN-based coatings mechanical properties.

Coating	Hardness (GPa)	Young's Modulus (GPa)
TiAlN (multilayer) [89,100]	29.0–37.0	370–462
TiAlSiN (multilayer) [94]	32.5–37.6	400–415
TiAlN/Ta [93]	29.0–33.0	300–325
Ti/TiAlN [88]	25.0–35.0	325–410
TiAlN/CrN [91]	37–41	420–475
TiAlN/TiN [90,96,98]	42–46	N/A
TiAlN/TiAl [92]	22.5–33.1	220–350
TiAlN/NbN [97]	16–30	433–606
TiCrAlCN/TiAlN [95]	23	N/A

The study of multilayered TiAlN-based coatings and their application in machining is not very abundant. However, the studies that are made about this topic focus primarily on the improvement of already existing multilayered TiAlN-based coating. There are some studies on novel coating structures such as the TiCrAlCN/TiAlN, but there is few information regarding its mechanical properties. Furthermore, machining case studies with the application of these are also sparse, these focusing on already existing multilayered coatings. Recent studies also focus on the improvement of coating's mechanical properties by introducing a novel structure, as seen in the case for TiAlSiN recently released [94]. This is also the case for recent research about TiAlN multilayer coatings, where layer thickness and residual stresses are tied to mechanical properties and wear behavior. The use of Ta is also studied for multilayered coatings, with the research made on this topic bearing better results in terms of mechanical properties and wear behavior using a first layer of Ta, it was concluded that coating's hardness and wear performance was significantly improved.

As presented in Section 2.1.2, the H/E ratio of the various analyzed coatings is going to be presented in Figure 31. Only coatings with complete information regarding this ratio will be presented.

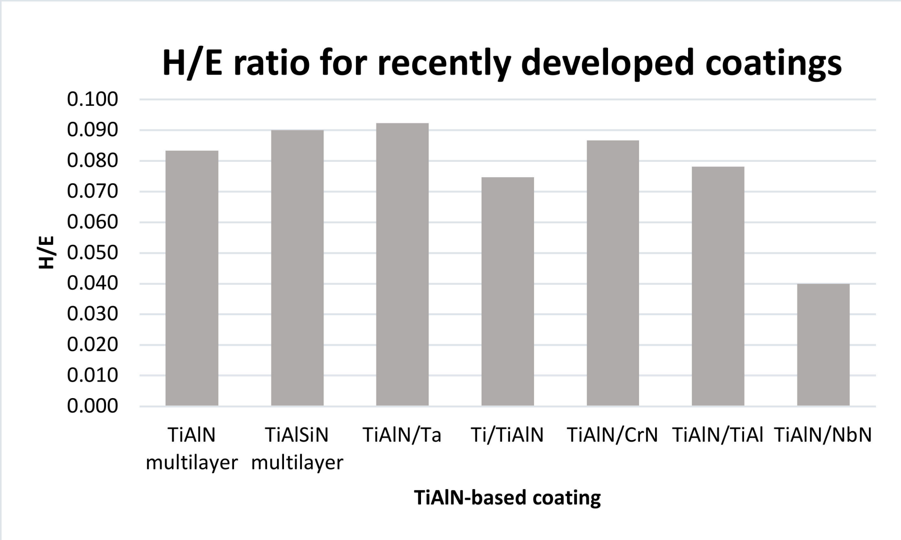

Figure 31. H/E ratio for recently researched multilayered TiAlN-based coatings.

As it was noted for monolayered coatings, the addition of certain elements such as Si, Ta and Cr significantly improve the wear behavior of the TiAlN based coatings. Recent research also shows that residual compressive stresses, microstructure and layer thickness also influence the wear behavior of the coatings, with TiAlN and TiAlSiN multilayered coatings achieving high values of hardness and Young's Modulus values, while also having a good performance in terms of wear.

2.3. Nanolayered TiAlN-Based Coatings

Recent studies made on coatings tend, in general, to be about nanostructured and nanocomposite coatings [39,43]. Nanolayered coatings, similarly to the multilayered coatings, have an increased crack propagation resistance. This is more intense on nanolayered coatings, due to the higher number of layers. Hardness values also tend to be higher on these types of coatings.

Regarding TiAlN-based coatings, the research trend is the same for other coating types, being more abundant in the area for nanolayered and nanocomposite TiAlN-based coatings. These recent papers tend to focus on the study of various novel coatings, based on the development of monolayered TiAlN-based coatings, more precisely, using elements that are tied to an improvement in mechanical properties such as Mo, Ta and Cr. In this section the various novel nanolayered/nanocomposite TiAlN-based coatings that are under development/study are going to be presented, mentioning their mechanical properties and wear behavior. Furthermore, as done in previous sections, the machining applications for these types of coatings are going to be presented for turning and milling. The various wear mechanisms that these tools are subject to are also going to be mentioned, presenting a comparison between coatings (when possible).

There is a current focus on the study of these types of coating over regular monolayered and multilayered coatings, with commonly known multilayered structures such as TiAl/TiAN [101], being attempted at a nanometric scale, with thinner layers conferring the coating with improved mechanical properties, such as high hardness, improved corrosion performance and high coating adhesion. As the layers are considerably thinner when compared to regular multilayered coatings, the number of layers is also higher in nanolayered coatings. This not only increases hardness, but also increases the crack propagation resistance of the coating. The influence of the layer thickness in nanolayered coatings is analyzed in the study performed by Wang et al. [102], where a TiN/TiAlN coating (another well-known multilayered architecture) is characterized in terms of mechanical properties and wear behavior. By controlling the rotation speed of coating deposition, the authors were able to control the thickness of deposited TiN and TiAlN layers. They determined the layer thickness value for highest mechanical properties (hardness and Young's Modulus), this value was found to be 13 nm. It was also noted that the wear behavior of the coating was improved for lesser thick layers, as this promoted crack propagation resistance. The coatings microstructure at different deposition rates can be observed in Figure 32.

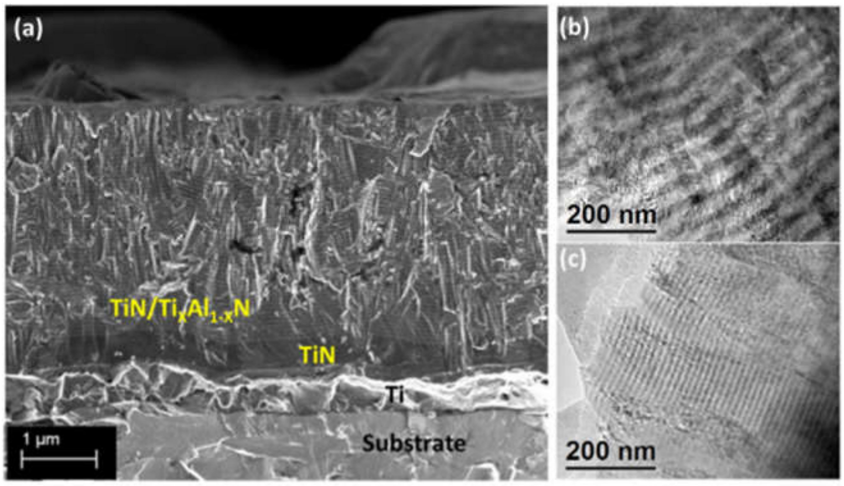

Figure 32. SEM cross-sectional image of TiN/TiAlN coatings for a rotation speed of 1 r.p.m. (**a**); TEM cross-sectional images for rotation of: 1 r.p.m. (**b**), 2 r.p.m. (**c**), presented by Wang et al. [102].

Another multilayered structure that has got some attention is the Al/TiAlN coating. In the study carried out by Liang et al. [103], an Al/TiAlN nanocomposite coating deposited on AZ91D magnesium alloy is analyzed. Similar to the previous study, here the authors studied the influence of different layer thickness on the mechanical properties and microstructure of the coating. In addition to the properties, the authors also analyzed the corrosion resistance of the coating. The authors produced four coatings with a thickness of 5 μm. The phases that form the nanocomposite film are TiN nanocrystal and amorphous AlN. These coatings had different interface periods, 100 nm, 200 nm, 300 nm and 400 nm. Regarding coating microstructure, it is columnar for 400 nm periods, however, it changes to multi-interfaces as the period is thinner. Hardness values reached their highest value for the lowest thickness period (100 nm), reaching 31.3 GPa. The authors also noted that the reduced thickness induced improved corrosion resistance, with the lowest thickness performing better in this regard as well. Layer thickness influence is a highly researched topic in nanolayered coatings, being related with an increase in mechanical properties (primarily hardness) and, as mentioned before, in nanolayered coatings the overall thickness of the coating improves hardness, as the high number of layers promotes a hardness increase. Additionally, this high number of layers in thick nanolayered coatings promotes a compressive stress relief on the coatings. The number of layers and their arrangement in a nanolayered coating also influences coating performance, which can be controlled by changing target arrangement (in deposition) and altering deposition time. This is highlighted in the study presented by Seidl et al. [104], which evaluated the influence of target arrangement in producing various AlCrN/TiAlTaN coatings. The control of the number of layers of AlCrN or TiAlTaN can influence greatly the coating's properties, with AlCrN (in this case) promoting better mechanical properties, while the TiAlTaN coating promoted a better oxidation resistance at higher temperatures. As seen in this study, the authors used a TiAlN coating with Ta addition, an element that is recently being researched for monolayered TiAlN-based coatings, as its addition is tied to improve mechanical properties.

The addition of Si is also very beneficial for the coating's mechanical properties, with some studies evaluating new structures such as the structure presented in [105], consisting of a first layer of TiAlN, followed by a nano multilayered TiAlN/AlCrSiN coating and finally, an outer layer of TiAlN coating. This coating's structure can be observed in Figure 33.

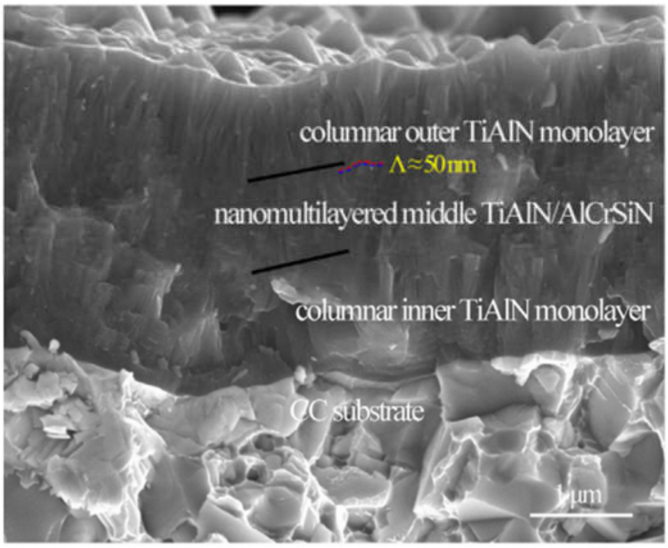

Figure 33. SEM cross-sectional image of TiAlN-(TiAlN/CrAlSiN)-TiAlN coating deposited on a cemented carbide presented by Xian et al. [105].

From the studies presented in Section 2.1, elements such as Mo and Y, when added to TiAlN coatings can significantly improve their hardness and Young's Modulus values, as well as their wear performance and corrosion resistance. In the study performed by Pshyk et al. [106], the novel nanocomposite (TiAlSiY)N and nanoscale (TiAlSiY)N/MoN multilayered coating obtained by arc-PVD are evaluated. The authors analyzed the microstructure, phase composition and mechanical properties of these coatings. Regarding the microstructure, the authors concluded that the multilayered coating had the preferred orientation, when compared to the monolayered nanocomposite coating. Moreover, the mechanical properties of the multilayered coating were better than the nanocomposite coating, showing values of 38.37 GPa and 392.5 GPa for hardness and Young's Modulus values, respectively. The (TiAlSiY)N/MoN coating also exhibited a better fracture toughness and a higher H/E ratio than the monolayered coating, thus having a better wear performance. Another study carried out by Kravchenko et al. [107] compare this novel coating with other similar structured coatings, namely, (TiAlSiY)N/CrN and (TiAlSiY)N/ZrN. These coatings were also obtained by arc-PVD and their mechanical properties were characterized. From that study, the authors concluded that the (TiAlSiY)N/MoN coating had higher values for hardness and Young's Modulus (35.9 GPa and 406.8 GPa, respectively) than the other coatings, with (TiAlSiY)N/CrN coating having 23.4 GPa and 300 GPa, and (TiAlSiY)N/ZrN having 22.1 GPa and 271 GPa, for hardness and Young's Modulus, respectively. However, the H/E and the plastic deformation indexes were very similar for all coatings, which means that these coatings (CrN and ZrN multilayer) have good tribological properties. Studies such as these [106,107] highlight the benefits of using these nano-multilayered coatings, especially for extreme tribological applications. Regarding TiAlN based nanolayered films with ZrN, Wang et al. [108] studied the influence of Zr_3N_4 on a nano multilayered TiAlN/Zr_3N_4. Additionally, the authors also studied the influence of layer Zr_3N_4 thickness in the coating's mechanical properties, and, as seen in the studies previously presented, thinner layers promote higher hardness and H/E ratio values. The authors also report that the Zr_3N_4 causes a significant increase in coating hardness (34.7 GPa) while retaining a very high toughness, conferring this coating with an excellent wear behavior. The hardness, Young's Modulus and H/E ratio variation of TiAlN/ Zr_3N_4 for different layer thicknesses can be observed in Figure 34.

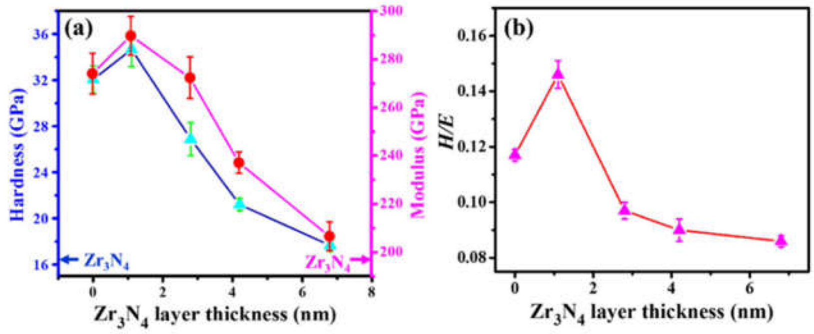

Figure 34. Hardness, Young's Modulus values (**a**) and H/E ratio values (**b**) for TiAlN/ Zr_3N_4 nano multilayered coatings, presented by Wang et al. [108].

The addition of Cu to tool coatings has some advantages, such as the reduction of friction coefficient as it is a soft and ductile material. The addition and use of these elements in nanocomposite coating has got some promising results, as seen in the study carried out by Chen et al. [109], where nanocomposite TiAlN/Cu coatings provided with varying percentages of Cu concentration (0–1.4 at % Cu concentration) are deposited by filtered cathodic arc ion plating. The authors have evaluated the coating's microstructure (Figure 35) and mechanical properties.

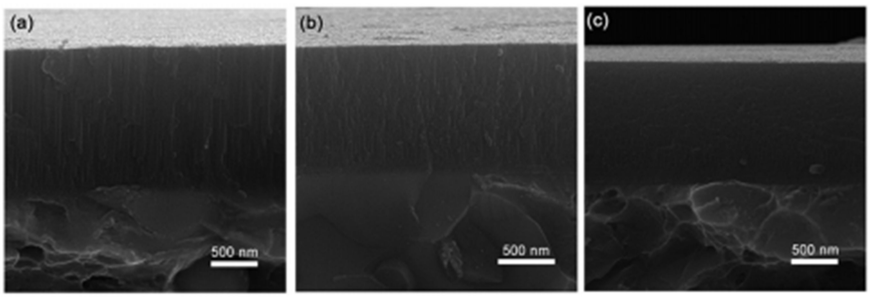

Figure 35. SEM cross-sectional images of TiAlN/Cu coatings with different concentrations of Cu: 0% at. % Cu (**a**); 0.8 at. % Cu (**b**); 1.4 at. % Cu (**c**), presented by Chen et al. [109].

From Figure 35, it can be observed that the addition of Cu results in a reduction in grain size, decreasing from 45 nm (in TiAlN) to 30 nm for the coating containing the highest Cu concentration. TiAlN presents a distinct columnar structure that gradually fades away with the addition of Cu. Regarding the coating's mechanical properties, there is a decrease in hardness value and Young's Modulus value with the increase in Cu concentration. There is also an influence on the friction coefficient, with the lowest value being obtained for a 0.8 at. % Cu concentration. Other Cu concentrations produced a higher friction coefficient, surpassing even the TiAlN coating. The addition of this element is an interesting topic, however, the sacrifice in mechanical properties does not seem to be relevant enough to use it to decrease in friction coefficient. However, the results presented in that paper show potential for the employment of Cu in coatings, as a decrease in friction coefficient is desirable, especially for applications such as machining. Still regarding the additions of softer elements to hard coatings such as TiAlN, in a similar study performed by Mejía et al. [110], the characterization of a TiAlN (Ag,Cu) nanocomposite coating is studied. As in the study previously mentioned here [109], the influence of the addition of different concentrations of (Ag,Cu) nanoparticles on the coating's mechanical properties and microstructure is studied. The addition of this softer element causes a grain refinement in the TiAlN coating's microstructure, changing from a columnar structure to an amorphous one with a smaller grain. Equal to the addition of Cu, the addition of these softer elements causes a decrease in mechanical properties (hardness and Young's Modulus value) and a decrease in friction coefficient. Additionally, the authors noted that with an increasing concentration of (Ag,Cu) the coating's residual compressive stresses would decrease.

2.3.1. Machining Applications and Coating Wear Behavior

In this section, the various studies regarding milling and turning applications of these types of coatings are going to be presented, mentioning the improvements that these types of coatings bring for machining. The wear behavior described in these studies is also going to be analyzed and described in this chapter.

Milling Process

Recent research on TiAlN-based coating's performance seems to be shifting to the use of these nanolayered and nanocomposite tool coatings. There have been many improvements recently on the development of new promising coatings for machining applications. However, the today's studies seem to focus on nanolayered and nanocomposite coatings containing elements such as Si and Cr, known as able to confer excellent mechanical properties and cutting performance to tool coatings. This recent paper presented by Geng et al. [111] studies the milling performance of TiSiN/AlTiN nanolayered composite film. The authors also evaluate de coating's microstructure and mechanical properties, which can be observed in Figure 36.

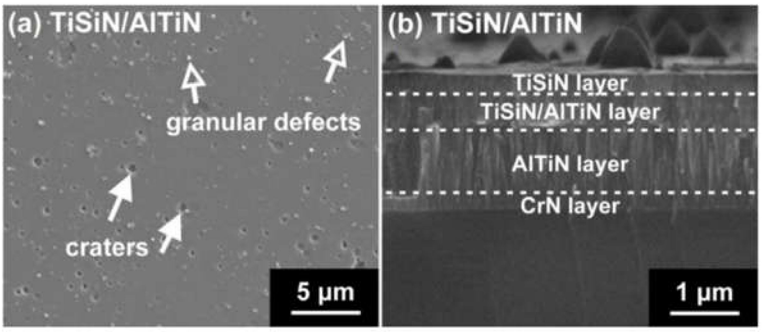

Figure 36. Surface (**a**) and SEM cross-sectional image (**b**) of TiSiN/AlTiN film, presented by Geng et al. [111].

Regarding the coating's mechanical properties, the registered peak values for hardness and Young's Modulus were 41.7 GPa and 340 GPa, respectively. These coatings were deposited onto 4-fluted end-mill with a 6-mm diameter and were subsequently employed in the dry milling of SKD 11 tool steel. The tool's wear was analyzed after the milling operations, and it was reported that the main wear mechanism was abrasion, as seen in Figure 37.

The authors noted that the TiSiN/AlTiN-coated tools showed little to no adhesion of SKD 11 to the coating's surface and the tools' edges. This resulted in a reduction of machining forces and cutting temperature, thus significantly improving the tool's life. Furthermore, there is a slight reduction in wear rate for a machining temperature of 400 °C. This study highlights the wear benefits that come from the employment of these coatings in machining.

As seen in the previous Section 2.3 (Nanolayered TiAlN-based coatings), multi nanolayered coatings with thinner layers exhibit an increase in mechanical properties (primarily hardness) and in wear behavior (low wear rate). This is also related to tool life, as presented by Teppernegg et al. [112]. Here, the authors studied a nano multilayer coating consisting of TiAlN and CrAlN sublayers with different thicknesses (10, 30, 100 and 300 nm), seen in Figure 38. These coatings are deposited onto inserts and their mechanical properties are evaluated; these are then employed in the milling of 42CrMo4 steel.

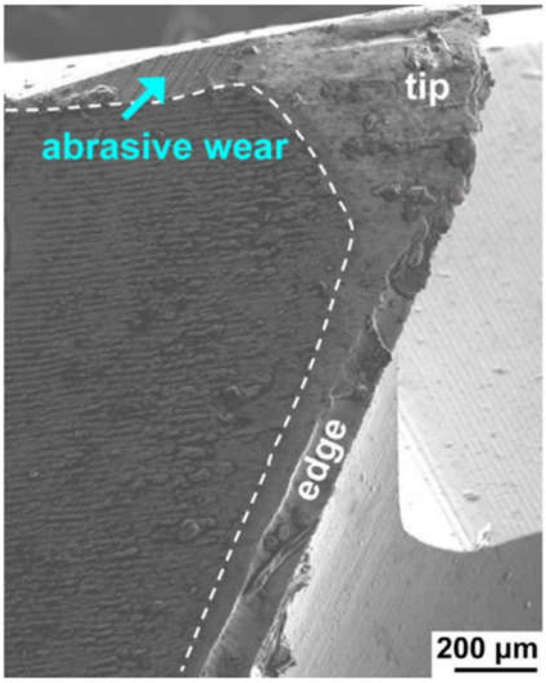

Figure 37. SEM images of the flank wear sustained bu TiSiN/AlTiN-coated tools after dry milling of SKD 11, presented by Geng et al. [111].

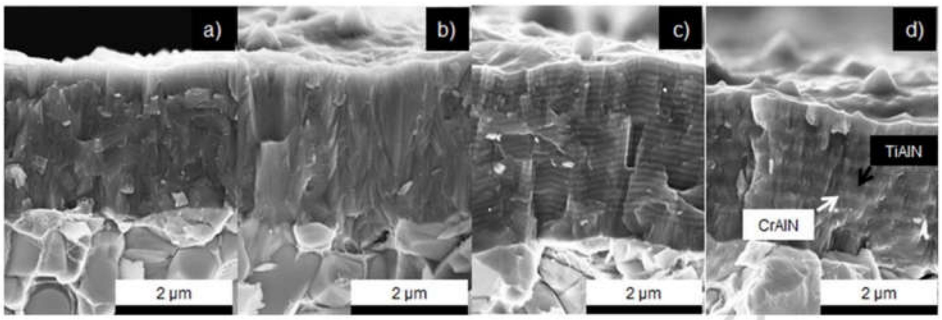

Figure 38. SEM cross-sectional image of the multilayered coatings with differing sublayer. 10 nm (**a**), 30 nm (**b**), 100 nm (**c**), 300 nm (**d**), presented by Teppernegg et al. [112].

It was noticed that an increase in Al content promoted higher hardness values being it related to cutting performance. Thus, the coating's that presented a higher Al content performed better in the milling tests. The sublayer thickness did not influence the hardness greatly, however, in terms of tool life this was not the case. The authors reported that with increased sublayer thickness the tool life would decrease. They were able to determine optimal sublayer thickness as seen in the Figure 39.

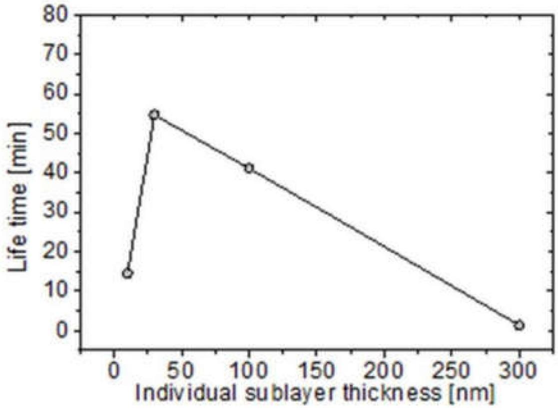

Figure 39. Tool life for the various layer thicknesses tested for the TiAlN/CrAlN nano multilayer coating, presented by Teppernegg et al. [112].

All the tested coatings exhibit the same type of wear. Coating failure occurs due to abrasion on the flank, causing coating erosion and delamination thus exposing the substrate. The other type of wear presented by the tools is thermal fatigue, this generating comb-cracks appearing on the coated inserts. These cracks can be seen in Figure 40.

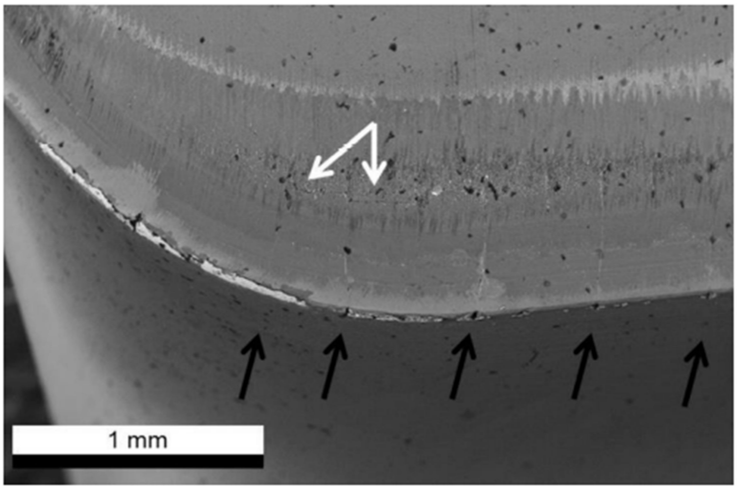

Figure 40. SEM image of the coated insert's cutting edge, the black arrows mark the position of comb-cracks and the white arrows mark the position of cracks that are parallel to the cutting edge, presented by Teppernegg et al. [112].

The employment of TiAlCrSiYN/TiAlCrN has also seen some studies lately, with Chowdhury et al. [113,114] evaluating the mechanical properties of this coating for various coating architectures and differing interlayer thicknesses. The authors also employ these coatings in the dry milling of stainless steel at a machining speed of 600 m/min. As seen in previous studies, the thinner the interlayer thickness is, the higher the hardness is. Chowdhury et al. [113,114] also compare these multilayered coatings with monolithic TiAlCrSiYN and TiAlCrN coatings. It was concluded that the nanolayered coatings, with optimized interlayer thickness produced the best results in terms of cutting performance and wear behavior, indicating that these types of nanolayered coatings are an excellent choice for extreme machining applications.

Turning Process

Similarly, to the research presented for the use of nanolayered and nanocomposite coatings in milling, for the turning process research focuses on coatings with Cr and

Si additions. These elements confer the coatings with excellent mechanical properties, and they improve the cutting performance significantly (especially when combined with TiAlN-based coatings). The use of these elements in nanolayered coatings has even more potential, increasing even more these properties and the cutting performance of coated tools, especially by extending the tool-life [115]. In the study conducted by Sui et al. [116] the performance of TiAlN/CrN coatings with different bilayer periods is evaluated in the high-speed turning of TC4 titanium alloy at 100 m/min. Bilayer periods between 12 nm and 270 nm were tested, and the influence of these periods on coating microstructure can be observed in Figure 41.

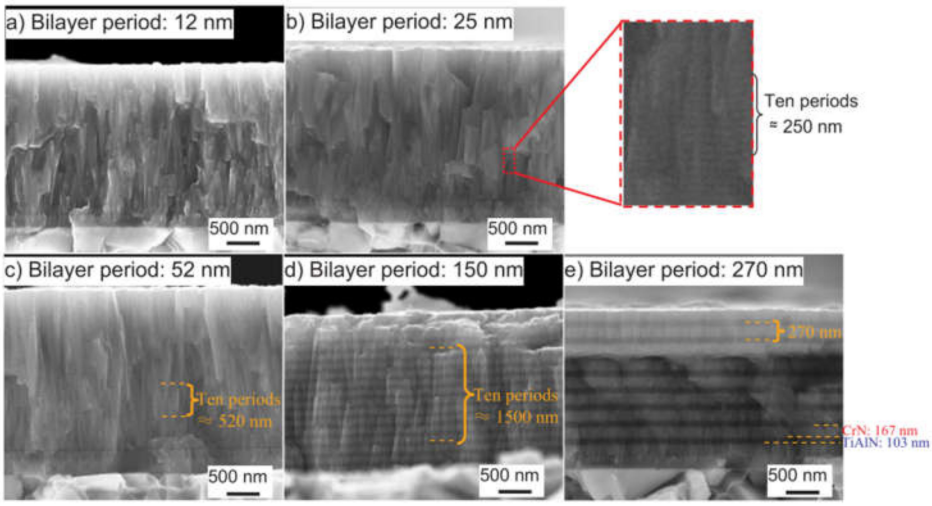

Figure 41. SEM cross-sectional image of the TiAlN/CrN coatings with different bilayer periods: 12 nm (**a**), 25 nm (**b**), 52 nm (**c**), 150 bm (**d**) and 270 nm (**e**), presented by Sui et al. [116].

With an increase in bilayer period, an increase in the coating's hardness was observed. This is due to a grain refinement that occurs with thinner layers. However, for the thinnest bilayer period, the hardness was also very high, such as the values obtained for the bilayer period of 270 nm. The authors also registered a higher wear rate for the thinner bilayer period (12 nm), with the thickest (270 nm) showing the best wear rate values. Regarding the wear mechanisms sustained by the tools, they were primarily abrasion and coating delamination. Although the tools experienced the same type of wear, the tool coated with the coating provided with the thickest layers exhibited less severe wear.

Still regarding the turning performance of nanolayered coatings, in the study developed by Zhang et al. [117], a comparison between AlTiN monolayered coating and AlTiN/AlCrSiN nano multilayered coatings is made. Furthermore, various nanolayered coatings were deposited with differing modulation period, that is, with differing layer thickness. The tested modulation period was between 4.2 nm and 17.8 nm. The various coatings mechanical properties were also determined. It was determined that the period of 8.3 nm (Figure 42) produced the best results in terms of hardness and Young's Modulus values for the coating (37.5 GPa and 486.9 GPa, respectively). Moreover, this coating exhibited the best values of H/E ratio and the best adhesion strength.

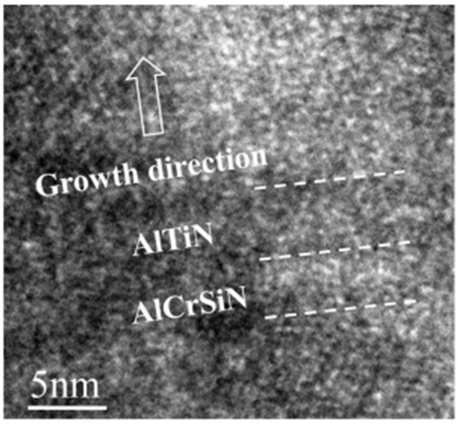

Figure 42. High-resolution TEM micrograph of AlTiN/AlCrSiN with a modulation period of 8.3 nm, presented by Zhang et al. [117].

The turning performance of these coatings was evaluated in the dry turning of SKD 11 tool steel at 250 m/min (cutting speed). The same wear mechanisms for AlTiN/AlCrSiN coated tools were reported, with abrasive and adhesive wear being reported as the main mechanisms. There was also the formation of BUE and some plastic deformation reported on the tool's rake face. The tool wear for the nanolayered coating with a modulation period of 8.3 nm can be observed in Figure 43. This coated tool exhibited the least wear rate of all coated tools, this is due to their high mechanical properties H/E ratio and high adhesion strength.

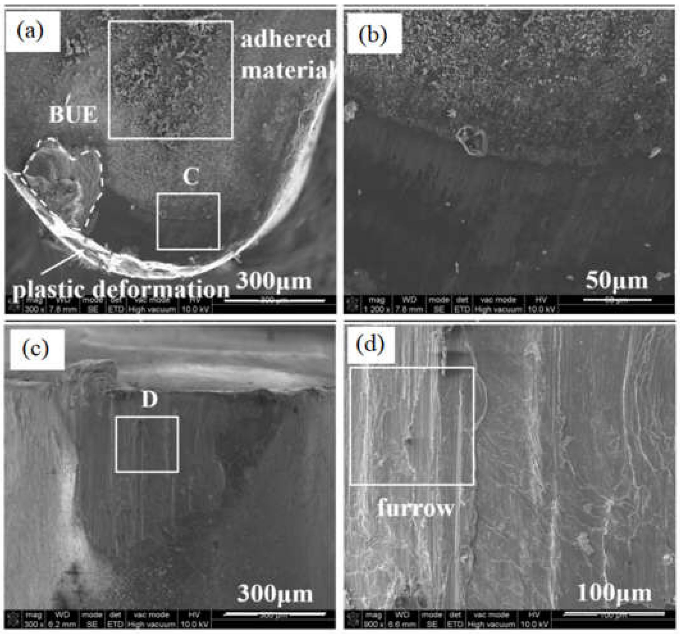

Figure 43. SEM image of the AlTiN/AlCrSiN (modulation period of 8.3 nm) coated tool's wear: rake face (**a**); magnified rake face (**b**), flank face (**c**), amplified flank face (**d**), presented by Zhang et al. [117].

From the studies presented, it can be concluded that abrasion is the common wear mechanisms sustained by nanolayered TiAlN-based coated tools. This is similar to the other types of coating's as well (monolayered and multilayered). However, the nanolayered coatings exhibit the highest tool-life values when compared to other types of coatings. This is due to their high count of very thin layers, conferring the coating with high hardness and high crack propagation resistance.

2.3.2. Comparison of the Coating's Mechanical Properties

The research trend for TiAlN-based coatings is heavily focused on the development and characterization of novel nanolayered and nanocomposite coatings. There have been improvements to already-known coating structures that are heavily employed, such as the TiN/TiAlN and Al/TiAlN. Studies conducted about these known structures focus on the improvement of mechanical properties and wear behavior by taking advantage of the nanolayered structure's benefits, such as an increased hardness value, reduced friction coefficient, reduced wear rate and high crack propagation resistance. These benefits become nanolayered and nanocomposite coatings very appealing, and therefore there are a higher number of papers done about this topic, than about regular multilayered coatings.

In Section 2.1., the addition of Mo to TiAlN-based coatings was covered. This element promotes an increase in the coating's mechanical properties and wear behavior. This was also observed in nanolayered and nanocomposite coatings, showing satisfactory results in creating coatings with high toughness and hardness values. The mechanical properties from the coatings that were mentioned in the previous subsubsection are going to be presented in Table 5.

Table 5. Hardness and Young's Modulus values for the nanolayered and nanocomposite TiAlN-based coatings.

Coating	Hardness (GPa)	Young's Modulus (GPa)
TiN/TiAlN [102]	31.5–42.5	417–520
Al/TIAlN [103]	23.0–31.0	N/A
(TiAlSiY)N/MoN [106,107]	36.0–38.0	395–406
(TiAlSiY)N/ZrN [107]	21.1–22.7	265–275
(TiAlSiY)N/CrN [107]	22.1–23.4	289–302
AlCrN/TiAlTaN [104]	32.0–42.0	N/A
TiAlN/ZrN [107,108]	22.0–36.0	210–290
TiAlN/Cu [109]	24.0–29.0	320–350
TiAlN(Ag,Cu) [110]	6.7–15.2	140–216
AlTiN/AlCrSiN [117]	28.5–31.0	410–450
TiSiN/TiAlN [115]	33.0–39.0	550–570
TiAlN/CrAlN [112]	25.0–30.0	N/A
TiAlCriSiYN/TiAlCiN [113,114]	24.0–33.0	430–475

It can be seen from the number of coatings presented in Table 4 alone, that there is considerably more research being made in novel coating development for these types of coatings when compared to monolayered and multilayered TiAlN-based coatings. Once again, it can be seen that the use of Mo increases significantly the coatings mechanical properties. There is some research, however, made about the improvement of already known structures. In regard to the TiN/TiAlN, a very high value of hardness was achieved, due to the nanolayered coating's properties.

Regarding these coating's wear behavior, (TiAlSiY)N/MoN showed great potential with very high values of hardness and good Young's Modulus values, becoming the types of coating that are very appealing for extreme applications, such as where wear is very intense. Some satisfactory results also come from the use of ZrN on the coatings, especially when coupled with TiAlN, achieving incredible mechanical properties. Figure 44 shows the H/E ratio of the coating analyzed in Section 2.3.

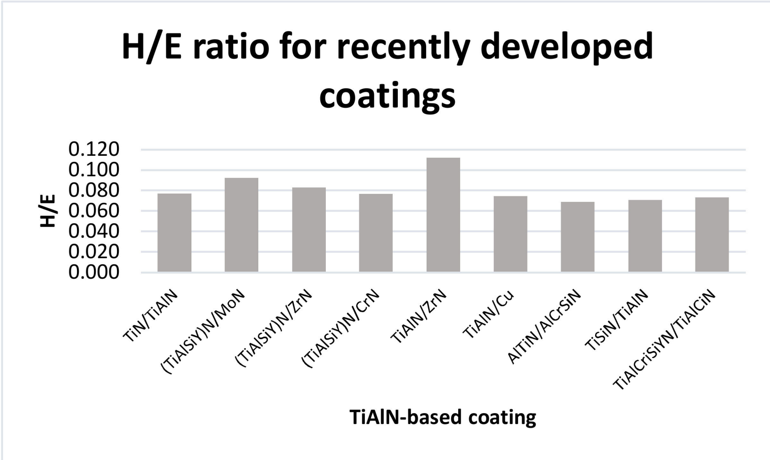

Figure 44. H/E ratio for recently researched nanolayered and nanocomposite coatings.

From analyzing the H/E ratios of the various coatings the TiAlN/ZrN coating has an incredibly high ratio, due to its mechanical properties. Indeed, this coating showed an excellent wear behavior, making it very promising for machining applications. Although there is variation of these ratios, only the TiAlN/ZrN coating ratio does not vary too much, an indicator that the wear performance of the nanolayered and nanocomposite coatings is superior to that of monolayered and multilayered TiAlN based coatings.

3. Machining Conditions and Tool Wear Mechanisms for TiAlN Based Coatings

Most of the research made about the TiAlN-based coatings regarding machining applications, is usually done about hard-to-machine materials. In this section, the various papers presented in Section 2 will be analyzed, presenting the materials that are currently being used in TiAlN based coating's testing. There are two sections, one for milling and another one for turning.

3.1. Milling Process

The Table 6 summarizes the various coatings used to machine a certain material, the range of machining speeds used and the main wear mechanisms of the coating.

Table 6. Materials machined by TiAlN-based coatings, applied in milling.

Material	Coating	Wear Mechanisms	Machining Speed Range [m/min]
Tool steels [70,71,74,97,111–114]	TiAlN	-Adhesion -Abrasion	40–600
	TiAlSIN	-Ploughing -Abrasion	
	CrTiAlSiN	-Thermal cracking -Abrasion	
	TiSiN/AlTiN	-Abrasion	
	TiAlN/CrAlN	-Micro-cracks -Abrasion	
	TiAlN/NbN	-Adhesion -Abrasion	

Table 6. *Cont.*

Material	Coating	Wear Mechanisms	Machining Speed Range [m/min]
Titanium alloys [72,75,76,96]	TiAlN	-BUE -Abrasion -Adhesion	9.6–173
	AlTiN	-Adhesion -Abrasion	
	TiAlN/TiN	-Adhesion -Abrasion -BUE	
Nimonic 75 [77]	TiAlN	-Coating chipping	13
Inconel 690 [73]	TiAlN	-Adhesion -Abrasion	60

As it was already concluded, the main wear mechanisms suffered while milling is abrasion and adhesion. For the milling of tool steel, abrasion is more predominant, however, for titanium alloys adhesion is more frequent. It is also important to note that multilayered and nanolayered tend to not suffer as much from adhesion problems.

3.2. Turning Process

Next, as in the previous section, the various coating used in the turning of various materials are going to be presented (Table 7), as well as the machining speeds that were used during testing.

Table 7. Materials machined by TiAlN-based coatings, applied in turning.

Material	Coating	Wear Mechanisms	Machining Speed Range [m/min]
Tool steels [81,83,98,100,117]	TiAlN	-Adhesion -Abrasion	120–500
	AlTiN	-Abrasion -Chipping	
	AlTiCrN	-Abrasion -Adhesion -BUE	
	TiAlN/TiN	-Abrasion -BUE	
Titanium alloys [82,115,116]	TiAlSiN	-Abrasion -BUE	100
	TiAlN/CrN	-Abrasion -Coating delamination	
	TiSiN/TiAlN	-Abrasion	
Inconel [78–80,99]	TiAlN	-Abrasion -Adhesion -BUE	30–120
	AlTiN	-Abrasion	
	TiN/TiAlN	-Abrasion	

The main wear mechanisms sustained by TiAlN-based coated tools when turning is abrasion and BUE. The studies about the employment of these coatings on turning operations, similarly to the ones for milling, focus on the machining of tool steel, titanium alloys and Inconel alloys.

Regarding the machining of Inconel, there is a clear advantage in having a higher concentration of Al in the coating, as it is related to the reduction of adhesive damage when machining these alloys.

4. Current Research Trends of TiAlN-Based Coatings

An analysis of current research about TiAlN-based coatings has been made and presented in this paper. Developments regarding monolayered, multilayered and nanolayered coating are currently being made, with a clear focus on the study of the addition of certain elements to TiAlN-based coatings in order to improve them. There are also studies made about the development of new coatings, such as self-lubricating coatings. As seen in the first chapter, the use of solid lubricants can significantly improve the performance of the coated tool [5]. This nanocomposite coating proves to have great potential, especially due to its low friction coefficient (due to self-lubricating behavior) which results in reduced wear behavior.

Still regarding recent research trends of TiAlN based coatings, similarly to the other coating type, there seems to be a focus on the study and development of nanolayered and nanocomposite coatings as presented in the previous chapters. These coatings have very high hardness values, due to the high number of layers, conferring super-hardness to these types of coatings (more than 40 GPa). There is also quite a lot of research done about these super-hard coatings (that do not need to be nanolayered as seen in [59]). These TiAlN-based super-hard coatings have better cutting performance when compared to the other regular TiAlN based coatings. This is due to their high hardness, a careful architecture of the coating's microstructure [118] and addition of some elements such as Mo [59] and Ta [119].

Regarding the research made on doping elements, it seems to be a popular topic, there are quite a lot of studies about the influence of certain elements in TiAlN-based coatings, with some yielding very satisfactory results. The use of Mo in coatings is well documented, with these coatings containing Mo, such as MoSeC coatings [120]. Mo addition not only improves the coating's mechanical properties, such as hardness and Young's Modulus [59,106,107], but also improves the friction coefficient of the coating, which promotes a better tool-life (reducing wear rate) [121,122]. There are some studies conducted about the reduction of wear coefficient of coatings, such as the ones using Cu and Ag [109,110] as doping elements. As it was observed, the addition of these elements resulted in a decrease in the coating's wear coefficient, but also hindered its mechanical properties, as it caused a reduction of hardness in the coatings. Mo is quite popular as it offers an increase in the coating's mechanical properties and improves the wear behavior of the coating, as seen in [106,107]. Moreover, it can be used in multilayer architecture, to be applied under the form of nitrides, such as MoN. The development of these low-friction coatings that can perform in rough conditions is collecting some attention, as seen in the paper presented by Bondarev et al. [123], where the MoSeC coating is paired with TiAlN based coating: TiAlSiCN. This super-hard coating (with about 41 GPa of hardness) had a comb-like structure that confers a high-thermal stability [124] and can be tailored to have a high oxidation resistance [125]. When this coating is paired with the MoSeC coating, which presents low friction coefficient [120], a very hard coating with an excellent wear behavior can be achieved. The authors [123] evaluated the wear behavior of TiAlSiCN/MoSeC coatings and have found that the addition of MoSeC caused a reduction in the hardness values registered in [124]. However, this addition highly improved the wear performance of these coatings, reducing the friction coefficient and improving the wear behavior at higher temperatures (up to 300 °C). Studies such as these show that the employment of Mo in coatings is quite beneficial, thus making it a popular research topic. Another element that as seen some research is Si, as the use of this element is quite popular in machining applications, especially for the TiAlSiN coating, which exhibit better mechanical properties and wear behavior than the TiAlN coating [65]. Its employment is quite beneficial, being used in some monolayered coatings, such as the CrTiAlSiN [71], and in some multilayered architectures [94], and nanolayered coatings [106,107,113,114]. As seen from the studies presented above [123–125] the TiAlSiCN coating has a very high thermal stability and excellent mechanical properties. From the study presented in [123], its employment in multilayered architectures also brings some benefits in terms of wear behavior. In the study performed by Golizadeh et al. [126], the authors evaluate the thermal stability and oxidation resistance of SiBCN/TiAlSiCN and AlOx/TiAlSiCN coatings. It was concluded that the base oxidation resistance and thermal stability of the TiAlSiCN coating were improved when using the multilayer coatings, with the AlOx/TiAlSiCN coating exhibiting the highest performance of all the coatings. Sill regarding doping elements of TiAlN-based coatings, some of these that are currently under research are Ta [63,119] and Y [63], yielding satisfactory results in terms of wear behavior and mechanical properties. There are, also, some novel coatings that use Ru [62,84] in their composition, which are also showing some promising results, however the amount of research in this matter is not as abundant as the other elements.

As previously mentioned, the nanolayered and nanocomposite coatings exhibit increased mechanical properties (presenting very high values of hardness generally) and wear behavior making them very appealing for the machining industry. New coatings have been developed, based on the research made about additive elements for monolayered coatings. Once again, the employment of Mo is under study for extreme applications, this time on nanocomposite coatings [106,107]. Still regarding the research made on nanolayered coatings, many studies are being made on the influence of layer thickness in coating's mechanical properties and cutting performance [39]. Furthermore, improvements are being made to already known coating architecture such as the TiAlN [89–100], TiAlSiN [65,94], TiAlN/TiN [90,96,98] and Al/TiAlN [103], with studies presenting increases in the coating's performances by employing methods to control layer thickness or concentration of phases, such as TiN and Al.

Regarding the machining applications that these coatings are applied to, from the analyzed research papers presented in this review, it is noticed that the coatings are mainly used in turning and milling operations. It was noticed that there are many research papers about milling operations using the TiAlN-based coated tools. However, for both machining cases, it was found that there is a large interest in the study of the wear performance of these coatings in the cutting of steels [70,71,74,81,83,97,98,100,111–114,117], titanium alloys [72,75,76,82,96,115,116] and Inconel [73,78–80,99]. This is due to these alloys being employed in the aeronautical industry, making the study of the machinability of these materials quite interesting. The applied coatings are usually novel nanocomposite coatings or already known structures (aforementioned) that have been improved in some way, being noticed that the coatings structure highly improves the wear behavior of these coatings (as previously mentioned). In the presented studies, the wear mechanisms are also evaluated, as there is a great interest in knowing how these coatings perform.

5. Concluding Remarks

In this paper, an analysis of recent research on TiAlN-based coatings applied to machining was performed. The main research topics about monolayered, multilayered and nanolayered and nanocomposite coatings were presented, mentioning the new developments made about these coating types, their benefits for the coating's mechanical properties, wear and cutting behavior. A comparison of these coating's mechanical properties was also made, as a way to link these to the coating's wear behavior. These coating's main applications were also analyzed and presented, mentioning the main wear mechanisms that these coated tools suffered when machining various types of material.

It was found that, regarding monolayered coatings, the research was primarily about the study of doping elements (as previously mentioned), with Mo additions yielding very satisfactory results. These additions promoted an increase in the coating's hardness, elastic modulus and toughness, thus promoting a slow wear rate for TiAlN-based coatings containing Mo. This was also registered for other elements such as Ru, Zr and Ta. Regarding other type of coating architecture, the main focus of recent research appears to be nanolayered and nanocomposite coatings, as their mechanical properties exceed those of the other coating types. Some of these coatings are super-hard, presenting hardness values above 40 GPa. This is very appealing as this promotes the wear performance of the coating, protecting it from abrasive wear. Furthermore, these coatings present very high crack resistance and very high toughness.

These types of coating architecture have an influence on the coating's properties and subsequently on their wear performance and cutting behavior. Properties that are of high importance and improve the coating's wear behavior are:

- Hardness;
- Toughness;
- H/E ratio (plasticity);
- Friction coefficient.

Regarding the coating's wear mechanisms, it was found that the main wear mechanisms present in milling are adhesion and abrasion, however, the employment of nanolayered coatings improves the adhesive damage suffered by the coatings. Regarding the coatings employed in the turning process, these usually suffer abrasive wear and BUE, with some coating's exhibiting adhesive wear. As for milling, the use of nanolayered and nanocomposite coatings improves the cutting behavior and tool life of the coated tools, with these types of coating outperforming regular monolayered TiAlN-based coatings.

Author Contributions: V.F.C.S.: investigation and writing original draft; F.J.G.D.S.: conceptualization, supervision, writing—review and editing; A.B.: supervision, writing—review and editing; G.F.P.: supervision, writing—review and editing; R.A.: supervision and formal analysis. All authors have read and agreed to the published version of the manuscript.

Funding: The present work was done and funded under the scope of project ON-SURF (ANI | P2020 | POCI-01-0247-FEDER-024521, co-funded by Portugal 2020 and FEDER, through COMPETE 2020-Operational Program for Competitiveness and Internationalization. LAETA/INEGI/CETRIB is acknowledge due to the support provided in all research activities.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest regarding this paper.

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