Article

Effect of Pressure and Temperature on Microstructure of Self-Assembled Gradient $\text{Al}_x\text{Ti}_{1-x}\text{N}$ Coatings

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Citation: Zalesak, J.; Todt, J.; Michalička, J.; Sartory, B.; Matko, I.; Lessiak, M.; Traxler, M.; Weißenbacher, R.; Pitonak, R.; Gammer, C.; et al. Effect of Pressure and Temperature on Microstructure of Self-Assembled Gradient $\text{Al}_x\text{Ti}_{1-x}\text{N}$ Coatings. *Coatings* **2021**, *11*, 416. <https://doi.org/10.3390/coatings11040416>

Academic Editor: Cecilia Bartuli

Received: 8 March 2021

Accepted: 1 April 2021

Published: 3 April 2021

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Abstract: The correlation between structural properties of Al-rich self-assembled nano-lamellar $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings and process parameters used during their chemical vapor deposition (CVD) remains unexplored. For this article, two gradient $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings were prepared by a stepwise increase in temperature and pressure in the ranges of 750–860 °C and 1.56 to 4.5 kPa during the depositions at a constant composition of the process gas mixture. The cross-sectional properties of the coatings were analyzed using X-ray nanodiffraction (CSnanoXRD) and electron microscopy. Experimental results indicate that the variation of the process parameters results in changes in microstructure, grain morphology, elastic strain, nanolamellae's chemistry and bi-layer period. At temperatures of ~750–800 °C and pressures of 2.5–4.5 kPa, preferably cubic nanolamellar grains are formed, whose microstructure correlates with the build-up of tensile stresses, which become relaxed in coating regions filled with nanocrystalline grains. CSnanoXRD superlattice satellite reflections indicate the period of the cubic Al(Ti)N-Ti(Al)N bilayers, which changes from 6.7 to 9 nm due to the temperature increase from 750 to ~810 °C, while it remains nearly unaffected by the pressure variation. In summary, our study documents that CVD process parameters can be used to tune microstructural properties of self-assembled $\text{Al}_x\text{Ti}_{1-x}\text{N}$ nanolamellae as well as the coatings' grain morphology.

Keywords: protective coating; TiAlN; self-assembly; LP-CVD; TEM; X-ray nanodiffraction

1. Introduction

Protective hard AlTiN coatings represent one of the most investigated coating systems as well as a common industrial standard for applications on cutting tools for dry and high-speed metal machining. The main interest in AlTiN, synthesized mainly by physical and chemical vapor deposition (PVD and CVD) techniques [1–3], resides in its superior oxidation resistance and high temperature hardness, compared to commonly used binary TiN and CrN coatings, which originates especially from the formation of beneficial Al_2O_3 and the age hardening effect [4].

In the last decade, a new type of $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings deposited by a low-pressure CVD (LP-CVD) process has been developed. These coatings, introduced in 2013 [5], attract attention because they break the Al-solubility limit of $x \approx 0.67$ in the face-centered cubic (FCC) rock salt (B1) phase commonly observed in PVD coatings [6,7]. This solubility limit has been explained by ab initio studies addressing the forming enthalpies of the FCC

and hexagonal $\text{Al}_x\text{Ti}_{1-x}\text{N}$ phases, which favor the formation of the latter one for $x \gtrsim 0.67$ in monolithic coatings [8]. The novel LP-CVD coatings exhibit a unique nano-lamellar microstructure based on alternating Al- and Ti-rich $\text{Al}_x\text{Ti}_{1-x}\text{N}$ lamellae, which are formed as a result of self-assembly during deposition [9]. The combination of high Al content in the FCC phase, and the nano-lamellar microstructure leads to superior thermal stability, oxidation resistance and mechanical properties, in comparison to traditional PVD-based $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings, as indicated in our previous reports [5,10,11].

The main focus of previous studies on self-assembled LP-CVD $\text{Al}_x\text{Ti}_{1-x}\text{N}$ -based coatings has been aimed at the characterization of mechanical and thermal properties as well as at the microstructural and chemical characterization of the self-assembled nanolamellae. Keckes et al. [5] characterized a coating with extremely high Al-content ($\text{Al}_{0.95}\text{Ti}_{0.05}\text{N}$), which consisted of alternating cubic Ti-rich and hexagonal Al-rich $\text{Al}_x\text{Ti}_{1-x}\text{N}$ nanolamellae within an h-AlN matrix. Although this coating was mainly composed of h-AlN, the presence of the nanolamellae greatly enhanced mechanical and oxidation properties in comparison to pure h-AlN [10]. The promising findings of these first studies initiated an iterative search for new LP-CVD process parameters to enhance the coating's mechanical properties. Zalesak et al. [12] reported on the evolution of nanolamellar microstructure, hardness and indentation modulus as a function of the Al/Ti ratio at the coating's cross-sections. Deposition conditions for a coating containing exclusively cubic nanolamellae were identified using correlative cross-sectional nanoanalytics, based mainly on nanoindentation and X-ray nanodiffraction experiments [12]. Excellent functional properties of the resultant cubic coating were demonstrated by Todt et al. [11], indicating a significantly higher thermal and mechanical stability in comparison to the often-referenced $\text{Al}_{0.62}\text{Ti}_{0.38}\text{N}$ coating from Ref. [13], which is prepared by a PVD method. Similar results have been reported also by Paseuth et al. [14], who analyzed preferred orientation, thermal stability and cutting performance of Al-rich cubic $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings prepared by LP-CVD. Cross-sectional microstructure, thermal stability, oxidation behavior, mechanical properties, and their mutual correlation were extensively analyzed by Tkadletz et al. [15,16] and Saringer et al. [17].

More recently, Ishigaki et al. [18] correlated the thickness of the nanolamellae with the Al content in the deposited $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings and indicated that the coatings with the highest Al content exhibited the most promising mechanical properties. Similarly, Uny et al. [19] studied self-assembled $\text{Al}_x\text{Ti}_{1-x}\text{N}$ CVD coatings deposited at a relatively high working pressure of 4 kPa and low carrier gas flow. These exhibited less pronounced nanolamellar microstructures resulting in lower hardness compared to the aforementioned results. Qui et al. [20] experimented with gas flow velocities and found that too high velocities resulted in co-growth of hexagonal and cubic phases and thus lead to an undesirable deterioration of mechanical properties.

The previous experimental reports indicated a complex correlation between the applied deposition conditions, the nanolamellar microstructure and the functional properties of the self-assembled nanolamellar CVD $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings. As indicated especially in the latter three of the abovementioned studies [18–20], significant differences in nano-lamellar morphology, thickness, chemistry, and phase composition have been observed and correlated especially with the precursor gases' flow, pressure, and ratio. Although the role of the applied precursor atmosphere has been evaluated extensively, the effect of other deposition parameters in the formation of the unique self-assembled microstructure remains largely unexplored. In this article, the focus lies on the characterization of the influence of the deposition temperature and the operating pressure on the microstructure, morphology, phases compositions, strain, and elemental compositions of LP-CVD $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings. For this reason, two gradient coatings were prepared at varying deposition conditions, to explore as many variabilities of the unique self-assembled nanostructured $\text{Al}_x\text{Ti}_{1-x}\text{N}$ system as possible.

2. Materials and Methods

2.1. Coating Deposition

A Bernex MT-CVD-300 (IHI Ionbond AG, Olten, Switzerland) medium temperature reactor was used for the deposition of two gradient $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings. As process gases, AlCl_3 , TiCl_4 , NH_3 , N_2 , and H_2 were applied. AlCl_3 was fabricated by a reaction of solid Al pellets (99.99% Al) with gaseous HCl. The coatings were deposited onto plain square cutting inserts made of WC-Co (6 wt.%) cemented carbide. Prior to the deposition, an approximately 100 nm thick TiN buffer layer was grown on the substrates in order to enhance coatings' adhesion.

For the first gradient coating (further denoted as *p-coating*), the overall pressure within the deposition chamber was varied in the range of 1.5–4.5 kPa, using 5 min long isobaric intervals during a total deposition time of 35 min. At the end of each interval, the pressure was increased using a diaphragm valve. The time evolution of the working pressure during the *p-coating*'s deposition is presented in Figure 1a. The CVD reactor deposition temperature was 800 °C.

The second gradient coating (further denoted as *T-coating*) was deposited at a constant overall pressure of 2.3 kPa with reactor temperature gradually increasing from ~750 to ~860 °C (measured in the center of the reactor). The time evolution of temperature with deposition time is plotted in Figure 1b.

Figure 1. Stepwise variations of (a) pressure and (b) temperature during the low-pressure chemical vapor deposition (LP-CVD) deposition of the *p*- and *T*-coating, respectively.

2.2. Electron Microscopy

Cross-sectional lamellae for transmission electron microscopy (TEM) were prepared by lift-out from both coatings using a Zeiss Auriga and a FEI Helios G3 dual beam focused ion beam (FIB) microscope. For the preparation, accelerating voltages varying from 30 to 2 kV and currents varying from 20 nA to 50 pA were used. In both cases, the entire thickness of each coating was preserved in the prepared lamellae.

Transmission Kikuchi diffraction (TKD) analysis was performed using a Zeiss LEO 1525 scanning electron microscope operated at an accelerating voltage of 20 kV and equipped with a Bruker e-flash FS electron back scatter diffraction (EBSD) detector. The scanning step size was set to 10 nm.

Scanning (STEM) imaging was performed using a JEOL 2200 FS microscope operated at 200 kV in STEM mode with a spot size of 0.5 nm. Images were recorded using high-angle annular dark-field (HAADF) and bright-field (BF) detectors and further treated using the Hugin image stitching software (2019.2.0).

Both, high-resolution (HR-TEM) imaging and energy-dispersive X-ray spectroscopy (EDX) STEM mapping were performed using, Cs-image-corrected TFS TITAN Themis 60–300 High-based microscope (Zaragoza, Spain) operated at 300 kV equipped with Super-X spectrometer with four 30 mm² windowless detectors. A probe current of ~1 nA was used for STEM-EDX mapping. Both HR-TEM and EDX data were collected and evaluated using the FEI Velox 2.7 software.

2.3. Cross-Sectional X-ray Nano-Diffraction

Scanning cross-sectional X-ray nanodiffraction (CSnanoXRD) experiments were carried out at the Nanofocus Extension of the beamline ID13 of the European Synchrotron (ESRF) in Grenoble, France, using a high-resolution multi-layer Laue lens-based X-ray optics setup that provided a beam cross-section of about 25 × 40 nm² at a photon energy of 12.6 keV [21]. For these experiments, cross-sectional coating-substrate slices with a thickness of ~50 µm were prepared from the two Al_xTi_{1-x}N/WC-Co specimens by cutting with a diamond wire saw and a subsequent mechanical polishing. At the beamline, the coating-substrate interfaces were aligned parallel to the incident beam, before scanning the coatings' cross-sections along the coatings' growth direction with a step size of ~20 nm. Diffraction images were collected in transmission on an Eiger X 4M area-sensitive X-ray detector (Dectris, Baden, Switzerland) and integrated using the software package pyFAI (version 0.20, ESRF, Grenoble, France) [22], while further evaluation such as peak fitting was carried out using custom Python scripts. The calibration of the detector geometry was performed using the pyFAI calibration tool [23] and a measurement of a National Institute of Standards and Technology (NIST) α-Al₂O₃ standard powder.

3. Results

3.1. Cross-Sectional Microstructure of the *p*- and *T*-Coating

In order to obtain representative information on the microstructural evolution across the thickness of the two coatings due to the gradual changes in pressure and temperature during their deposition (Figure 1), advanced electron microscopy techniques were applied. Cross-sectional micrographs from the *p*- and *T*-coating are presented in Figures 2 and 3. HAADF STEM micrographs in Figure 2a,c show the Z-contrast, where dark and bright regions correspond to Al- and Ti-rich regions, respectively. In the STEM micrographs in Figure 2b,d, darker regions correspond to stronger-diffracting areas. Additionally, transmission EBSD (tEBSD) data were recorded on the cross-sectional TEM lamellae prepared using FIB. Figure 3a,c shows where cubic FCC phase was successfully indexed (bright areas). Figure 3b,d indicates the in-plane orientations of individual cubic grains. The combination of Figures 2 and 3 allows for extracting information about the cross-sectional microstructural evolution.

Figure 2. Cross-sectional microstructure of the *p*- (a,b) and *T*-coatings (c,d) obtained using high-angle annular dark-field (HAADF) scanning TEM (STEM) (a,c) and bright-field STEM (b,d). The scale bar corresponds to 1 μm .

In the case of the *p*-coating deposited at 800 $^{\circ}\text{C}$ (Figures 2a,b and 3a,b), the initial growth, starting with the lowest pressure of 1.56 kPa, resulted in the formation of mainly hexagonal phase with very fine nanoscopic grains, which could not be indexed using tEBSD. Cubic grains containing nanolamellae are also present here in a small amount, and, with the increasing pressure, their concentration and diameter both increased gradually

towards the coating's surface (Figure 3b). Even at the highest pressure of 4.5 kPa, a small amount of hexagonal phase was still present in the coatings, as visible in Figure 3b. In other words, the higher pressure promoted the formation of relatively large cubic grains with angular shape and nanolamellar interior within the *p*-coating, as further discussed below.

Figure 3. Transmission electron back scatter diffraction (EBSD) from the *p*- (a,b) and *T*-coating (c,d). In (b,d), orientation maps show the in-plane orientation of cubic crystallites. In (a,b), the transmission EBSD (tEBSD) indexing reliability documents the occurrence and morphology of cubic grains at both coatings' cross-sections.

In the case of the *T*-coating deposited at a pressure of 2.3 kPa, (Figures 2c,d and 3c,d), the deposition started at a temperature of 750 °C, which resulted in the formation of elongated cubic grains filled with alternating Ti- and Al-rich nanolamellae. This microstructure is similar to the one reported for the heteroepitaxially grown $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coating in Ref. [9]. With increasing temperature, however, the size of the columnar cubic grains decreased, they became more equiaxed, but also more angular. Similarly, the cubic phase fraction within the coatings decreased continuously with increasing temperature, as can be seen in the tEBSD data presented in Figure 3d.

The electron microscopy data in Figures 2 and 3 indicate that the variation of temperature and pressure during the deposition of the two respective gradient coatings resulted

in the formation of varying grain microstructures, with columnar and nano-composite attributes, as well as with a varying ratio between cubic and hexagonal phases. In general, temperature and pressure seem to affect the coating inversely with respect to one another.

3.2. CSnanoXRD Analysis

CSnanoXRD [21] was used to evaluate various film thickness-dependent structural parameters of the gradient coatings, like phase composition, ratio between cubic and hexagonal phases, and the bi-layer period of the nanolamellae. The phase plots in Figure 4a,d (along with the data shown in Figure 1) indicate that the formation of FCC phases with distinctive $\text{Al}_x\text{Ti}_{1-x}\text{N}$ 111 and 200 reflections is favored at high working pressures in the *p-coating* and at low reactor temperatures in the *T-coating*. Complementarily, the hexagonal phase and its $\text{Al}_x\text{Ti}_{1-x}\text{N}$ 111, 002, and 101 reflections were observed mainly within the interface and surface regions of the *p-* and *T-coatings*, respectively, in clear agreement with the data presented in Figure 3. The relative intensities of the cubic and hexagonal reflections visible in Figure 4a,d were used to evaluate the ratio between cubic and hexagonal $\text{Al}_x\text{Ti}_{1-x}\text{N}$ phases. The data in Figure 4b,e document a gradual increase and decrease in the cubic phase fraction towards the *p-* and *T-coatings'* surfaces, respectively, asymptotically approaching the 100% cubic phase limit in both coatings.

Since the positions of the cubic and hexagonal reflections in Figure 4a,d change as a function of the coatings' thickness, it can be supposed that the lattice parameters of the phases were influenced by the *p* and *T* variation, even though the composition of the precursor gases during the deposition did not change. Another reason for the observed shifts of reflection positions (Figure 4a,d) can be the presence of elastic strain within the coatings. Therefore, assuming a biaxial stress state, in-plane elastic first-order strain was evaluated from the ellipticity of cubic $\text{Al}_x\text{Ti}_{1-x}\text{N}$ 200 and hexagonal $\text{Al}_x\text{Ti}_{1-x}\text{N}$ 100 reflections. The dependencies in Figure 4c,f indicate that significant tensile strains are present in the cubic phase-dominated regions of the two coatings, whereas in the bi-phase and hexagonal zones, the coating is nearly free from macro-strains or only slightly compressively strained. The presence of the tensile stresses in the cubic phase can be interpreted by the larger coefficient of thermal expansion (CTE) of cubic $\text{Al}_x\text{Ti}_{1-x}\text{N}$ (approximately $7.5 \times 10^{-6} \text{ K}^{-1}$) in comparison with the CTE of the substrate (approximately $6.5 \times 10^{-6} \text{ K}^{-1}$), resulting in the formation of tensile stresses after the coatings were cooled down from the deposition temperatures [24]. The nearly stress-free hexagonal phases in both coatings can be interpreted by the smaller CTE mismatch between the hexagonal $\text{Al}_x\text{Ti}_{1-x}\text{N}$ phase [24] and the substrate as well as by the composite nature of the respective coating regions. As the chemical composition of the phases determines their respective elastic properties, the conversion of the measured strains in Figure 4c,f to stresses has not been performed, but the highest observed tensile strains of ~ 0.0055 would correspond to approximately 2.0 GPa in pure TiN. Such a high value would be unrealistic in a bulk material, but due to the small grain size and nano-composite nature of the investigated samples, it seems plausible here.

Finally, clear superlattice satellite reflections were observed next to the cubic $\text{Al}_x\text{Ti}_{1-x}\text{N}$ 111 and 200 reflections in the coating segments rich in cubic phases, indicating a rather more strictly periodic nano-lamellar nanostructure (cf. Figure 4a,d). The apparent limit for the possibility to resolve the satellite reflections lies at about 80% cubic phase fraction (Figure 4b,e). The satellite reflections were used to evaluate the coatings' thickness-dependent superlattice period of the $\text{Al}(\text{Ti})\text{N}$ - $\text{Ti}(\text{Al})\text{N}$ bi-layers [9] within the cubic grains (Figure 4a,d). Essentially, the satellite reflections' spacing is inversely proportional to the bi-layer spacing, in a relationship similar to small-angle scattering. In the *p-coating*, the nano-lamellar period remained relatively constant in the range of 9.2–10 nm, whereas in the *T-coating*, a linear increase from 6.7 to 9 nm was observed proportionally to the increasing temperature (Figure 4c,f).

Figure 4. Results from scanning cross-sectional X-ray nanodiffraction (CSnanoXRD) indicate the evolution of phases across cross-sections of the *p*- (a) and *T*-coating (d). In (b,e), the cubic phase fraction is presented. In (c,f), cross-sectional evolutions of in-plane strains in cubic (prefix c) and hexagonal (prefix w) $\text{Al}_x\text{Ti}_{1-x}\text{N}$ phases, as well as the superlattice period of the cubic nanolamellae, are presented.

The structural data collected using CSnanoXRD unambiguously indicate that the variation of the pressure and/or temperature resulted in cross-sectional variations of lattice parameter, superlattice period, elastic strain, and fractions of cubic and hexagonal phases across the thicknesses of the two gradient coatings deposited using a constant composition of the process gas mixture.

3.3. Chemical and Structural Analysis of the Nanolamellae

The angular grains with cubic non-stoichiometric Al(Ti)N-Ti(Al)N bi-layers [9] represent the most interesting microstructural feature in the self-assembled nanolamellar $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings, which predetermine their functional properties like relatively high hardness and excellent thermal stability [11,15]. The cubic nanolamellae are formed from the gas phase on {100}-faceted surfaces of growing grains as a result of a sequential epitaxial overgrowth during oscillating chemical reactions, as extensively discussed in Ref. [9]. Currently, it is, however, unclear, why the growth of the grains eventually terminates and only grains of a limited length and/or size are formed [9]. To address this question, the chemical composition of the cubic grains and the terminating sublayers was investigated in detail using STEM-EDX and HR-TEM.

In Figure 5, detailed elemental maps collected from a representative nanolamellar region with cubic grains within the *p-coating* are presented. Al, Ti, and Cl maps and a line scan indicate a periodic variability in the composition of Al(Ti)N-Ti(Al)N bi-layers filling the cubic grains, as already discussed elsewhere [9,15]. In other words, the concentrations of Al and Ti change in an oscillatory fashion across the nanolamellar grains and the bilayers are non-stoichiometric [9]. Cl atoms are present in a small amount but clearly recognizable in the EDX spectra (not shown here). Comparatively smaller amounts of Cl were recorded for Al-rich regions (up to 0.5 at.%), while Ti-rich regions systematically contain higher content of Cl (up to 2 at.%). Interestingly, the cubic nanolamellar grains are always terminated (i) by an Al-rich nanolayer (indicated by dashed outline arrows in Figure 5), which is followed (ii) by an irregular polycrystalline region (indicated by solid outline arrows in Figure 5), which is rich in Ti and Cl and depleted in Al. This is confirmed in the HAADF STEM image in Figure 6, highlighting the terminal Al-rich nanolayers (dashed outline arrows) as well as the irregular polycrystalline region (solid outline arrows). The Al-rich layer appears dark in the chemically sensitive (Z-contrast) HAADF STEM image.

In Figure 7a, a HR-TEM micrograph from a representative terminal Al-rich nanolayer is presented (indicated by the arrows), which grows epitaxially on the cubic Ti(Al)N-Al(Ti)N bilayer structure. Moreover, in Figure 7b, a HR-TEM image filtered by an inverse fast Fourier transformation (FFT) from the rectangular region indicated in Figure 7a is presented along with FFTs of the representative cubic (Figure 7c) and hexagonal (Figure 7d) regions. The HR-TEM data indicate that the terminal nanolayer is hexagonal and that the switch from cubic to hexagonal $\text{Al}_x\text{Ti}_{1-x}\text{N}$ phase occurs abruptly.

In summary, the results presented in Figures 5 and 6 document that the formation of approximately 9 nm thick Al-rich nanolayers, terminating the cubic grains, is accompanied (i) by a sudden change in the chemical composition (with Al and Cl excess) (cf. Figure 5) as well as (ii) by a sudden switch in the crystal structure type from cubic to hexagonal (cf. Figure 7). The hexagonal Al-rich nanolayer is further followed by a polycrystalline hexagonal region, which is rich in Cl and Ti (cf. Figures 5 and 6). It should be noted that equivalent nanolamellar regions like those presented in Figures 5–7 were identified also in the *T-coating*. In other words, the cubic phase-dominated nanolamellar regions exhibited identical microstructural and chemical properties within both gradient coatings.

Figure 5. Representative STEM-energy-dispersive X-ray spectroscopy (EDX) maps show qualitative (a) Al, (b) Ti, and (c) Cl element distributions across representative cubic nanolamellar $\text{Al}_x\text{Ti}_{1-x}\text{N}$ grains. A line scan (d) was plotted using data integrated in a dashed box. Dashed outline arrows indicate the presence of Al-rich hexagonal nanolayers terminating cubic $\text{Al}_x\text{Ti}_{1-x}\text{N}$ grains, which are followed by polycrystalline Ti-rich and comparatively Cl-rich regions (indicated by solid outline arrows).

Figure 6. HAADF STEM micrograph from a representative cubic $\text{Al}_x\text{Ti}_{1-x}\text{N}$ grain. The dashed outline arrows indicate the terminating hexagonal Al-rich layers (cf. Figures 5 and 6) and the solid outline arrows show polycrystalline regions rich in Cl (cf. Figure 5).

Figure 7. High-resolution TEM (HR-TEM) micrograph (a) showing an interface between a cubic Ti(Al)N/Al(Ti)N nanolamella stack and the terminating hexagonal Al-rich nanolayer (indicated by dotted outline arrows). The inverse FFT filtered HR-TEM micrograph (b) obtained from the dashed region in (a) documents an abrupt switch in crystal structure from cubic to hexagonal, as documented also by the FFTs from the respective cubic (c) and hexagonal (d) regions.

4. Discussion

The aim of this study was to analyze possible variabilities of the unique self-assembled nanostructured $\text{Al}_x\text{Ti}_{1-x}\text{N}$ system featuring $\text{Al}(\text{Ti})\text{N}$ - $\text{Ti}(\text{Al})\text{N}$ bi-layers. The primary motivation was to understand if the variation of process temperature and pressure (at constant composition of the process gas mixture) can be used to tune morphological and structural properties of $\text{Al}_x\text{Ti}_{1-x}\text{N}$ grains and nanolamellae, i.e., the coatings' distinctive microstructure.

For this study, we decided to utilize a combinatorial strategy, on which we already have reported in our earlier studies related to this topic, especially for the self-assembled $\text{Al}_x\text{Ti}_{1-x}\text{N}$ system [12], considering both limitations and advantages of this approach. In both cases studied here (*p*- and *T*-coatings), the recorded changes in microstructure, phase and atomic composition must be interpreted carefully because the changes in process parameters could also influence deposition rates. Therefore, individual regions in the deposited coatings at specific film thicknesses cannot be attributed to exact deposition conditions like the applied pressure and temperature at a certain deposition time. Due to this reason, corresponding temperature and pressures values can only be estimated and might vary to a certain extent. On the other hand, most of the observed cross-sectional effects show clearly recognizable trends and thus can be correlated qualitatively with the changes in deposition conditions. In this way, the employed combinatorial approach was used to screen a large amount of process parameters and has revealed a great variability of microstructural and structural features within the graded self-assembled coatings.

4.1. Properties of *T*-Coating

In most previous studies [10–12], a deposition temperature of approximately 800 °C for self-assembled LP-CVD $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings has been used. At this temperature, the formation of homogeneous and predominantly cubic phase $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coatings has been reported. In the present study, a temperature interval of 750–860 °C was selected in order to further analyze the self-assembly process. We are aware of the possibility that the increasing of the working temperature during deposition process may have affected already deposited sublayers. On the other hand, so far published results on thermal stability [11,15] has shown only slight changes in the temperature interval, which was selected in our study (750–860 °C). Therefore, we do not expect trends observed in our study to be significantly affected by our deposition strategy.

At the cross-section of the *T*-coating, a great variability of microstructure, grain morphology, and phases was observed (Figure 2c,d, Figure 3c,d, and Figure 4d–f) as a result of the continuous temperature increase (Figure 1b). At a coating depth of roughly 2.5 µm, corresponding approximately to a deposition temperature of 800 °C, predominantly relatively large angular grains were formed, filled entirely with cubic self-assembled nanolamellar $\text{Al}_x\text{Ti}_{1-x}\text{N}$ (Figures 2–4). In the temperature range of 750–800 °C and at the respective coating depth range of 5–2.5 µm, the self-assembly process was dominated by the formation of cubic phases in elongated grains (Figure 2c,d and Figure 3c,d). Interestingly, the bi-layer period increased monotonously from approximately 6.7 to approximately 9 nm along with the increasing temperature. The in-plane elastic strains are relatively large compared to the fine-grained coating region within the coating depth range of 2.5–0 µm, which was deposited at the respectively highest deposition temperatures in the range of 800–855 °C. The application of these higher deposition temperatures resulted in the formation of a composite microstructure featuring a predominantly hexagonal $\text{Al}_x\text{Ti}_{1-x}\text{N}$ matrix phase.

It is interesting to observe that deposition temperature apparently plays a very important role in the formation of $\text{Al}(\text{Ti})\text{N}$ - $\text{Ti}(\text{Al})\text{N}$ bi-layers, which are formed as a result of a sequential epitaxial overgrowth during oscillating chemical reactions [9]. The results indicate that there is a relatively large temperature window, within which the reaction results in the formation of periodic cubic nanolamellae having a certain bilayer thickness range from 6.7 to 9 nm (Figure 4f). When the temperature is increased beyond a critical value, however, predominantly hexagonal phase is formed from the same process gas mixture. This effect might be interpreted by different temperature-dependent lattice parameters

of the Al(Ti)N and Ti(Al)N bilayer sublayers (Figure 7a). When they form, the coherent Al(Ti)N/Ti(Al)N bilayers are epitaxially grown one onto another, mutually stabilizing their cubic phase, while the respective layer thicknesses, stoichiometries, and coherency strains are within a limited kind of balance [9]. It can be supposed that there is a critical thickness of the bilayers, which, when exceeded, results in the collapse of the cubic phase and the formation of the hexagonal Al(Ti)N nanolayer (like in Figures 5 and 7). In other words, the coherency strains between the Al(Ti)N and Ti(Al)N sublayers become too large for bilayer thickness larger than approximately 9 nm and therefore, the cubic grains with this “sensitive” (in terms of stability) cubic phase are not further patterned.

4.2. P-Coating

The influence of deposition pressure is expected to be crucial, simply because $\text{Al}_x\text{Ti}_{1-x}\text{N}$ nanolamellar coatings so far have been achieved only by LP-CVD techniques, as opposed to more standard higher pressure CVD variants. The lowest pressure of 1.56 kPa applied in this study was selected based on hardware limitations. The investigated deposition pressure interval of 1.56–4.5 kPa (Figure 1a) can be divided into 3 parts, based on characteristics of the coating. The lowest third ≤ 2.5 kPa (within a depth range of 4.5–3 μm) is characterized by a very dominant hexagonal phase fraction. Here, the composite microstructure contains only a small portion of nanoscopic cubic grains, dispersed within a nanocrystalline hexagonal matrix. The in-plane elastic strains measured by CSnanoXRD in this region are negligible in both phases (Figure 4c), probably because of the composite nature of the material. In the next third, at applied deposition pressures of 2.5–3.0 kPa, corresponding to depths of 3.0–1.5 μm within the coating, the cubic phase fraction exceeds approximately 0.6 and tensile in-plane strains develop rapidly as the coating grows further, while the amount of hexagonal Al-rich matrix phase is reduced significantly. Finally, at deposition pressures of 3.5–4.5 kPa and a depth range of 0–1.5 μm , the remainder of hexagonal phase is still present only in the terminating layers of otherwise fully cubic and nanolamellar grains, while the in-plane strain of the cubic phase stays rather constant at a high level and the bi-layer period does not change significantly. It is interesting to note, however, that the bi-layer period in the *p-coating* of 9.2–10 nm is somewhat higher than the apparently critical bi-layer thickness in the *T-coating* of 9 nm. This can be explained by the lower deposition pressure used for deposition of the *T-coating* of only 2.3 kPa, as compared to the 3.5–4.5 kPa present in this upper part of the *p-coating* and thus it is clear that both pressure and temperature (along with the process gas mixture) have to be considered as crucial for microstructural stability.

Another interesting feature of the self-assembly process is the formation of the terminating Al-rich as well as Ti-depleted nanolayers (indicated by dashed outline arrows in Figures 5–7), which are followed by polycrystalline regions rich in Cl and Ti and depleted in Al (cf. solid outline arrows in Figures 5 and 6). The Ti compositional deficit in the terminating nanolayer grown onto cubic grains suggests also an instability of the oscillating growth reaction, which can be caused by a momentary Ti depletion of the process gas at the growing grain's surface. As a result, a hexagonal Al-rich nanolayer is formed and AlCl_3 precursor gas is consumed preferentially. In consequence, the further coating growth results in the formation of Ti-rich and Al-depleted regions. It is currently unclear, why this region is polycrystalline and, additionally, why the Cl concentration is increased. One possible explanation for the Cl enrichment could be the fact that if AlCl_3 is depleted and therefore there is an over-abundance of TiCl_4 , also the Cl content of the atmosphere close to the growth surface is increased and hence more Cl is incorporated into the coating.

5. Conclusions

Experimental results obtained from two gradient coatings indicate that the variation of process temperature and pressure, at constant composition of the process gas mixture, results in changes in coatings microstructure, structural properties, and grain morphology.

Within the *T-coating* deposited in the temperature range of 750–860 °C, a cubic phase microstructure with Al(Ti)N-Ti(Al)N nanolamellae is formed mainly at temperatures below approximately 800 °C. The temperature changes during deposition result in the formation of a gradient microstructure with both, microscopic columnar and also nanoscopic angular grains. Interestingly, temperature influences the thickness of the self-assembled nano-lamellae, and there is a threshold of approximately 9 nm, above which hexagonal nanolamellae are formed at the applied constant deposition pressure of 2.3 kPa.

Within the *p-coating*, prepared using a deposition pressure ranging from 1.56 to 4.5 kPa, a nanocrystalline and hexagonal microstructure is formed at lower pressures. At pressures greater than or equal to approximately 2.5 kPa, the cubic phase starts to be more favored in comparison to the hexagonal phase (at the applied constant deposition temperature of 800 °C). A further increase in pressure results in the formation of a mostly cubic microstructure and, at the highest pressures, a very slight decrease in the nanolamellar bi-layer period was observed, while values range slightly higher at 9.2–10 nm.

An intricate inter-dependence between deposition pressure, temperature, bi-layer thickness and in-plane film strain in the cubic phase has been observed and rationalized in terms of the stability of the growth process of the nanolamellar structures. Further investigations into the lamellar packets' chemistry revealed the prevalence of hexagonal Al-rich terminating layers and corroborate the hypothesis of an oscillating growth reaction.

In summary, the results document that the LP-CVD process parameters can be used effectively to tune structural properties of self-assembled $\text{Al}_x\text{Ti}_{1-x}\text{N}$ nanolamellae as well as the overall grain morphology. To obtain a fuller understanding of the forming structures, additional variation studies at particularly interesting points in parameter space should be conducted, such as in phase/structure stability transition regions. Based on existing knowledge about the relationships between structure and functional properties, our findings will enable the synthesis of wear-resistant coatings with increased performance and lifetime.

Author Contributions: Conceptualization, J.Z., J.T., R.P. and J.K.; experimental characterization and data evaluation, J.Z., J.T., J.M., B.S. and I.M.; sample design, M.L., M.T., R.W. and R.P.; writing—original draft preparation, J.Z., J.T. and J.K.; supervision, C.G.; funding acquisition, project administration, and supervision, J.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Österreichische Forschungsförderungsgesellschaft mbH (FFG), Project No. 864828, “Tough_TiAlN.” CzechNanoLab project LM2018110 funded by MEYS CR is gratefully acknowledged for the financial support of the sample FIB fabrication and TEM measurement at CEITEC Nano Research Infrastructure.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mitterer, C. PVD and CVD hard coatings. In *Comprehensive Hard Materials*; Elsevier Ltd.: Amsterdam, The Netherlands, 2014; Volume 2, pp. 449–467, ISBN 9780080965284.
2. Endler, I.; Höhn, M.; Herrmann, M.; Pitonak, R.; Ruppi, S.; Schneider, M.; van den Berg, H.; Westphal, H. Novel aluminum-rich $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings by LPCVD. *Surf. Coat. Technol.* **2008**, *203*, 530–533. [[CrossRef](#)]
3. Kowalski, S. Assessment of the possibility of the application of a CrN + OX multi-layer coating to mitigate the development of fretting wear in a press-fit joint. *Wear* **2018**, *398–399*, 13–21. [[CrossRef](#)]
4. Mayrhofer, P.H.; Hörling, A.; Karlsson, L.; Sjöln, J.; Larsson, T.; Mitterer, C.; Hultman, L. Self-organized nanostructures in the Ti-Al-N system. *Appl. Phys. Lett.* **2003**, *83*, 2049–2051. [[CrossRef](#)]
5. Keckes, J.; Daniel, R.; Mitterer, C.; Matko, I.; Sartory, B.; Koepf, A.; Weißenbacher, R.; Pitonak, R. Self-organized periodic soft-hard nanolamellae in polycrystalline TiAlN thin films. *Thin Solid Films* **2013**, *545*, 29–32. [[CrossRef](#)]

6. PalDey, S.; Deevi, S.C. Single layer and multilayer wear resistant coatings of (Ti,Al)N: A review. *Mater. Sci. Eng. A* **2003**, *342*, 58–79. [\[CrossRef\]](#)
7. Kutschej, K.; Mayrhofer, P.H.; Kathrein, M.; Polcik, P.; Tessadri, R.; Mitterer, C. Structure, mechanical and tribological properties of sputtered $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings with $0.5 \leq x \leq 0.75$. *Surf. Coat. Technol.* **2005**, *200*, 2358–2365. [\[CrossRef\]](#)
8. Holec, D.; Rachbauer, R.; Chen, L.; Wang, L.; Luef, D.; Mayrhofer, P.H. Phase stability and alloy-related trends in Ti-Al-N, Zr-Al-N and Hf-Al-N systems from first principles. *Surf. Coat. Technol.* **2011**, *206*, 1698–1704. [\[CrossRef\]](#)
9. Zalesak, J.; Holec, D.; Matko, I.; Petrenec, M.; Sartory, B.; Koutná, N.; Daniel, R.; Pitonak, R.; Keckes, J. Peculiarity of self-assembled cubic nanolamellae in the TiN/AlN system: Epitaxial self-stabilization by element deficiency/excess. *Acta Mater.* **2017**, *131*, 391–399. [\[CrossRef\]](#)
10. Todt, J.; Pitonak, R.; Köpf, A.; Weißenbacher, R.; Sartory, B.; Burghammer, M.; Daniel, R.; Schöberl, T.; Keckes, J. Superior oxidation resistance, mechanical properties and residual stresses of an Al-rich nanolamellar $\text{Ti}_{0.05}\text{Al}_{0.95}\text{N}$ coating prepared by CVD. *Surf. Coat. Technol.* **2014**, *258*, 1119–1127. [\[CrossRef\]](#)
11. Todt, J.; Zalesak, J.; Daniel, R.; Pitonak, R.; Köpf, A.; Weißenbacher, R.; Sartory, B.; Mitterer, C.; Keckes, J. Al-rich cubic $\text{Al}_{0.8}\text{Ti}_{0.2}\text{N}$ coating with self-organized nano-lamellar microstructure: Thermal and mechanical properties. *Surf. Coat. Technol.* **2016**, *291*, 89–93. [\[CrossRef\]](#)
12. Zalesak, J.; Todt, J.; Pitonak, R.; Köpf, A.; Weißenbacher, R.; Sartory, B.; Burghammer, M.; Daniel, R.; Keckes, J. Combinatorial refinement of thin-film microstructure, properties and process conditions: Iterative nanoscale search for self-assembled TiAlN nanolamellae. *J. Appl. Crystallogr.* **2016**, *49*, 2217–2225. [\[CrossRef\]](#)
13. Chen, L.; Paulitsch, J.; Du, Y.; Mayrhofer, P.H. Thermal stability and oxidation resistance of Ti-Al-N coatings. *Surf. Coat. Technol.* **2012**, *206*, 2954–2960. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Paseuth, A.; Yamagata, K.; Miura, A.; Higuchi, M.; Tadanaga, K. Deposition and analysis of Al-Rich c- $\text{Al}_x\text{Ti}_{1-x}\text{N}$ coating with preferred orientation. *J. Am. Ceram. Soc.* **2017**, *100*, 343–353. [\[CrossRef\]](#)
15. Tkadletz, M.; Hofer, C.; Wüstefeld, C.; Schalk, N.; Motylenko, M.; Rafaja, D.; Holzschuh, H.; Bürgin, W.; Sartory, B.; Mitterer, C.; et al. Thermal stability of nanolamellar fcc- $\text{Ti}_{1-x}\text{Al}_x\text{N}$ grown by chemical vapor deposition. *Acta Mater.* **2019**, *174*, 195–205. [\[CrossRef\]](#)
16. Tkadletz, M.; Lechner, A.; Schalk, N.; Sartory, B.; Stark, A.; Schell, N.; Saringer, C.; Mitterer, C.; Czettel, C. Influence of spinodal decomposition and fcc $\rightarrow$ w phase transformation on global and local mechanical properties of nanolamellar CVD fcc- $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings. *Materialia* **2020**, *11*. [\[CrossRef\]](#)
17. Saringer, C.; Tkadletz, M.; Stark, A.; Schell, N.; Czettel, C.; Schalk, N. In-situ investigation of the oxidation behavior of metastable CVD- $\text{Ti}_{1-x}\text{Al}_x\text{N}$ using a novel combination of synchrotron radiation XRD and DSC. *Surf. Coat. Technol.* **2019**, *374*, 617–624. [\[CrossRef\]](#)
18. Ishigaki, T.; Tatsuoaka, S.; Sato, K.; Yanagisawa, K.; Yamaguchi, K.; Nishida, S. Influence of the Al content on mechanical properties of CVD aluminum titanium nitride coatings. *Int. J. Refract. Met. Hard Mater.* **2018**, *71*, 227–231. [\[CrossRef\]](#)
19. Uny, F.; Blanquet, E.; Schuster, F.; Sanchette, F. Ti-Al-N-Based Hard Coatings: Thermodynamical background, CVD deposition, and properties. A Review. In *Coatings and Thin-Film Technologies*; IntechOpen: London, UK, 2019.
20. Qiu, R.; Forslund, A.; Bäcke, O.; Iyer, A.H.S.; Sattari, M.; Janssen, W.; Manns, T.; Kümmel, J.; Ruban, A.; Stiens, D.; et al. Effects of gas flow on detailed microstructure inhomogeneities in LPCVD TiAlN nanolamella coatings. *Materialia* **2020**, *9*, 100546. [\[CrossRef\]](#)
21. Keckes, J.; Daniel, R.; Todt, J.; Zalesak, J.; Sartory, B.; Braun, S.; Gluch, J.; Rosenthal, M.; Burghammer, M.; Mitterer, C.; et al. 30 nm X-ray focusing correlates oscillatory stress, texture and structural defect gradients across multilayered TiN-SiO_x thin film. *Acta Mater.* **2018**, *144*, 862–873. [\[CrossRef\]](#)
22. Kieffer, J.; Karkoulis, D. PyFAI, a versatile library for azimuthal regrouping. *J. Phys.* **2013**, *425*, 202012. [\[CrossRef\]](#)
23. Ashiotis, G.; Deschildre, A.; Nawaz, Z.; Wright, J.P.; Karkoulis, D.; Picca, F.E.; Kieffer, J. The fast azimuthal integration Python library: PyFAI. *J. Appl. Crystallogr.* **2015**, *48*, 510–519. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Bartosik, M.; Holec, D.; Apel, D.; Klaus, M.; Genzel, C.; Keckes, J.; Arndt, M.; Polcik, P.; Koller, C.M.; Mayrhofer, P.H. Thermal expansion of Ti-Al-N and Cr-Al-N coatings. *Scr. Mater.* **2017**, *127*, 182–185. [\[CrossRef\]](#)