Solid state formation of Ti$_4$AlN$_3$ in cathodic arc deposited (Ti$_{1-x}$Al$_x$)N$_{y}$ alloys

Isabella Schramm, C. Pauly, Mats P Johansson Jöesaar, Per Eklund, J. Schmauch, F. Muecklich and Magnus Odén

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Transformation mechanism from Ti$_2$AlN to Ti$_4$AlN$_3$

1. Ti$_2$AlN
2. Intergrown structure Ti$_6$Al$_2$N$_4$
3. Ti$_4$AlN$_3$

HAADF STEM image
Solid state formation of Ti$_4$AlN$_3$ in cathodic arc deposited (Ti$_{1-x}$Al$_x$)$_N$ alloys

I.C. Schramm$^{1,2,*}$, C. Pauly$^2$, M.P. Johansson Jõesaar$^{1,3}$, P. Eklund$^4$, J. Schmauch$^5$, F. Mücklich$^2$, and M. Odén$^1$

* Corresponding author: isasc@ifm.liu.se

1. Nanostructured Materials, Department of Physics, Chemistry, and Biology, Linköping University, Linköping, Sweden
2. Chair of Functional Materials, Department of Material Science, Saarland University, Saarbrücken, Germany
3. SECO Tools AB, Fagersta, Sweden
4. Thin Film Physics Division, Department of Physics, Chemistry, and Biology, Linköping University, Linköping, Sweden
5. Experimental Physic, Department of Physics, Saarland University, Saarbrücken, Germany

Reactive cathodic arc deposition was used to grow substoichiometric solid solution cubic $c$-(Ti$_{1-x}$Al$_x$)$_N$ thin films. The films were removed from the substrate and then heated in an argon environment to 1400 °C. Via solid state reactions, formation of MAX phase Ti$_4$AlN$_3$ was obtained. Additional phases such as Ti$_2$AlN, $c$-TiN, $w$-AlN, Al$_5$Ti$_2$ and Al$_3$Ti were also present during the solid state reaction. Ti$_4$AlN$_3$ formation was observed in samples with an Al metal fraction $x < 0.63$ and a nitrogen content $0.4 < y < 0.6$. Regardless of the initial composition, formation of Ti$_4$AlN$_3$ started in Ti$_2$AlN crystal plates in the temperature range between 1200 - 1400 °C. Accompanying the onset of Ti$_4$AlN$_3$ was the presence of an intermediate structure identified as Ti$_6$Al$_2$N$_4$, consisting of alternating layers of intergrown Ti$_2$AlN and Ti$_4$AlN$_3$ phases with a half-unit-cell stacking. We suggest that the formation of Ti$_4$AlN$_3$ occurred via intercalation of aluminum and nitrogen along the basal plane accompanied by a simultaneous detwining process. In addition we propose that this formation mechanism can be used to obtain MAX phases of high $n$ order.

Keywords: MAX phase, intergrown phase, thin films, solid state reaction, intercalation
1. Introduction

$M_{n+1}AX_n$ phases (“MAX” phases, $n = 1 - 3$) are nanolaminated hexagonal materials composed of a transition metal $M$-element (Ti, Zr, V, …), an A-element (Al, Si, Ge, …), and C or N (or both) as X-element [1]. The structure consists of $M_6X$ octahedral layers separated by A-element layers. Depending on the number ($n$) of $M$ layers separated by A layers the nomenclature will be $M_2AX$ ($n = 1$), $M_3AX_2$ ($n = 2$) or $M_4AX_3$ ($n = 3$). Due to their layered structure, MAX phases present a rather complex interatomic bonding, where the $M$-$A$ bonds are weaker than the $M$-$X$ bonds. This results in materials with a combination of metal and ceramic properties which are elastically stiff, oxidation and thermal shock resistant, machinable, thermally and electrically conductive, etc. [1,2]. MAX phase materials are valuable in the shape of thin films for technical applications including electrical contacts, protective coatings, and low friction surfaces, among others. The technologies used to make thin film MAX phases can be divided in three main groups: physical vapor deposition, chemical vapor deposition, and solid state reaction synthesis [3,4]. Solid state reactions are further divided in two subgroups: one based on reactions between substrate and thin film, and the other on reactions of the coating. The most important example of the first subgroup is $\text{Ti}_3\text{SiC}_2$ formation as ohmic contacts on $\text{SiC}$ [5–7]. The second type involves deposition of a $M$-$A$-$X$ film of appropriate composition in a metastable state, amorphous [8–10] or multilayer [11–15], followed by annealing to form the MAX phase.

Two MAX phases have been reported experimentally in the Ti-Al-N system, $\text{Ti}_2\text{AlN}$ and $\text{Ti}_4\text{AlN}_3$. The hypothetical $\text{Ti}_3\text{AlN}_2$ phase predicted to be metastable by DFT calculations performed by Holm et al. [16] has not been synthesized and is unlikely to exist [3,11]. Only $\text{Ti}_2\text{AlN}$ has been obtained as a thin film via solid state reactions [11,12,17] and reactive
sputter deposition [18–21]. Even though $\text{Ti}_4\text{AlN}_3$ was synthesized and characterized in the late 90’s [22,23], it has not been obtained as a thin film.

We report a method for obtaining $\text{Ti}_4\text{AlN}_3$ via solid state reactions of a nitrogen deficient monolithic cubic solid solution $c-(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ thin film synthesized by cathodic arc deposition in an industrial system. We show that it is possible to form $\text{Ti}_4\text{AlN}_3$ for a large range of aluminum to titanium ratio and nitrogen compositions, and that the amount of $\text{Ti}_4\text{AlN}_3$ formed can be tuned. Formation of $\text{Ti}_2\text{AlN}$ is required in order to achieve $\text{Ti}_4\text{AlN}_3$ since $\text{Ti}_2\text{AlN}$ acts as a template above 1200 °C. Finally, our results suggest a route for formation of high $n$ order MAX phases.

2. Experimental details

An industrial scale PVD cathodic arc deposition system, MZR-323 by Metaplas, Germany (now Oerlikon Metaplas GmbH), was used to grow nitrogen deficient $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ coatings. The nitrogen content of the coating was controlled by varying the $\text{N}_2$ ratio of an Ar/$\text{N}_2$ gas mixture between 25 and 33 % during growth. The total gas pressure was fixed at 2 Pa, and a dc bias of - 30 V was used. Three circular cathodes of $\text{Ti}_{1-x}\text{Al}_x$ ($x = 0, 0.55$ and $0.67$) with a diameter of 100 cm were mounted facing a rotating cylinder. The thin films were grown on Fe foils to a thickness of about 3 µm at a rate of 0.1 µm per minute and a temperature of ~ 450 °C.

Mechanical grinding of the coated Fe foils was followed by dissolution of remaining iron in concentrated HCl solution to obtain flake-like particles of the coating material. The coating flakes were recovered, cleaned with distilled water and acetone, and finally ground in a ceramic mortar. The powder preserved a flake-like shape, its crystal structure and composition were not affected by this process [24].
Powder annealing treatments under argon atmosphere were performed in a differential scanning calorimeter, STA 449C by Netsch, Germany. The annealing temperatures used were from 1000 to 1400 °C, with no isothermals and always using as-prepared powder for each temperature. Powder placed in an alumina crucible was heated at a rate of 20 K per min under an argon flow of 50 ml/min. Out gassing for one hour at 250°C was always performed just prior to the heating.

Powder X-ray diffractometry (XRD) was performed in an Empyrean diffractometer (PANalytical, The Netherlands) using Cu-Kα radiation in focusing Bragg-Brentano configuration with low background optics. Diffractograms were recorded at room temperature and a silicon zero diffraction plate was used to hold the powder.

Scanning electron and focused ion beam microscopy (SEM/FIB) (Helios NanoLab 600, FEI, United States) was used for scanning transmission imaging (in SEM), fabrication of site specific thin lamellas for transmission electron microscopy (TEM) and atom probe tomography (APT) tips. A standard lift out technique was used for the APT tips [25], and no deviation in the procedure was necessary because of the flake-like shape of the powder particles. STEM-in-SEM imaging in this instrument was performed at 30 kV.

3D chemical composition was obtained by local electrode atom probe tomography (LEAP 3000 X HR, Cameca, France) in laser mode. The laser was set to a frequency of 200 kHz and a pulse energy of 0.5 nJ. Measurements were carried out at a cryogenic temperature of 60 K and an evaporation rate of 5 ions per 1000 laser pulses. Data analysis was performed with the software package IVAS (version 3.6.14, Cameca). Reconstruction parameters were obtained individually for each tip by using Kingham curves [26] and post measurement SEM images. The evaporation field obtained was 40 V per nm and the image compression factor ranged from 3.4 to 4.0.
Transmission electron microscopy (TEM) and scanning TEM (STEM) were used to characterize the microstructure of the annealed powder in more detail. TEM analysis was performed using a JEM 2010 model of JEOL (Japan) at an acceleration voltage of 200 kV. TEM/STEM analysis was carried out using a cold field emission gun JEOL JEM-ARM 200F at 200 kV equipped with a STEM Cs corrector (CESCOR, CEOS GmbH, Germany). For STEM, the high angle annular dark-field (HAADF) detector was used. TEM thin lamellae were produced using the SEM/FIB and further thinning was performed with an Ar Ion gun (Nanomill Mod. 1040, Fischione, United States) at a beam current of 125 pA for 20 min at a tilt angle of ±10°.

3. Results

3.1 As-deposited state

Ternary composition map of the investigated (Ti$_{1-x}$Al$_x$)$_3$N$_y$ coatings is shown in Figure 1. Samples are represented by dots and labeled A to F. For reference, the compositions corresponding to the MAX phases Ti$_2$AlN and Ti$_4$AlN$_3$, and horizontal lines representing fixed nitrogen/metal ratios are included. The notation (Ti$_{x-1}$Al$_x$)$_3$N$_y$ is obtained with $x = \frac{Al}{(Ti + Al)}$ and $y = \frac{N}{(Ti + Al)}$ where Ti, Al, and N are the elemental concentrations. The alloy compositions were measured by atom probe tomography. In addition to the main elements, small amounts of impurities are also present in the analysis, i.e. oxygen, carbon, argon, and gallium originating from the background pressure of the industrial deposition system and the FIB sample preparation [25]. The total impurities concentration is less than 1.0 at. %.

Chemical distribution of the main elements, Ti, Al and N, in as-deposited samples and their deviation from a random distribution were obtained using frequency distribution analysis and
by calculating the Pearson coefficient ($\mu$) [27], as shown in Table 1. The Pearson coefficient addresses qualitatively the composition deviation, where a value of 0 indicates a completely random distribution and 1 indicates complete segregation. For comparison, two samples grown under similar conditions from a previous publication [28], containing a higher nitrogen content and same metal fraction as sample C, are included and labeled with a star. Metal and nitrogen segregation were observed for all as-deposited samples, being more pronounced for samples with low nitrogen content. A stronger aluminum segregation is apparent, while Ti retains a close to random distribution with more titanium present in the global composition, i.e. sample F. These results are consistent with the $c$-$(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ x-ray peak broadening seen in Figure 2.

The x-ray diffractograms of nitrogen deficient flake-like powder $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ samples in their as-deposited state are shown in Fig. 2. Results indicate that all samples are solid solutions with a cubic B1 crystal structure $c$-$(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$, similar to what has been seen for coatings with higher N content [28,29]. No MAX phase peaks were detected in the low 20 range between 5 and 30° (not shown). Increasing Ti content (reduction in x) corresponds to an increase of the lattice parameter, which shifts the $c$-$(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ peaks to lower diffraction angles and consistent with previous results for $y = 1$ [30]. In samples A and B, $x > 0.48$, additional wurtzite $w$-AlN and cubic $c$-TiN diffraction peaks are present. $w$-AlN peaks are broad and shifted to lower angles since $w$-AlN also contains titanium. In addition, the 111 and 200 diffraction peaks for $c$-$(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ display different intensity ratios depending on the N content. The 111 peak increases in intensity when the nitrogen content is reduced, which is consistent with a change in the structure factor caused by a reduced N lattice site occupancy when nitrogen vacancies are present [28,31]. The structure factor change is observed as a gain in the XRD peak intensity ratio 111 to 200 and the variation of the 111 to 222 ratio. These changes are stronger than what the weak crystallographic texture gives.
3.2 High temperature reactions

In order to trace the phase transformation route, flake-like powder samples were annealed at different temperatures from 1000 to 1400 °C. Figure 3 shows room temperature x-ray diffractograms recorded after annealing and only samples presenting substantial differences are shown.

Sample A, (Ti$_{0.27}$Al$_{0.63}$)N$_{0.46}$, with a high Al content shows the highest phase fraction of Ti$_2$AlN at 1000 °C. As-deposited w-Al(Ti)N peaks shift toward w-AlN positions due to the low solubility of Ti atoms, corroborated by the formation of c-TiN simultaneously. When annealed at higher temperatures, the intensity of Ti$_2$AlN and c-(Ti$_{0.27}$Al$_{0.63}$)N$_{0.46}$ peaks decrease and completely disappear at 1300 °C. At 1400 °C, only c-TiN and w-AlN peaks are present.

1000 °C XRD results of sample C, (Ti$_{0.52}$Al$_{0.48}$)N$_{0.40}$, shows formation of intermetallic Al$_5$Ti$_2$ and a shift of c-(Ti$_{0.52}$Al$_{0.48}$)N$_{0.40}$ peaks toward c-TiN position by Al depletion. Further annealing leads to the transformation of Al$_5$Ti$_2$ to Al$_3$Ti, further purification of c-TiN, formation of w-AlN, and a dominant presence of Ti$_2$AlN. Between 1200 and 1400 °C, Ti$_2$AlN and Ti$_4$AlN$_3$ coexist with the additional presence of a third intermediate phase, accompanied by a decrease in c-TiN and an increase in Al$_3$Ti peaks. Finally at 1400°C, Ti$_2$AlN and the intermediate phase are gone, and Ti$_4$AlN$_3$ is the dominant phase. Secondary phases, Al$_3$Ti, c-TiN, w-AlN, and small amounts of Al$_2$O$_3$, are also present.

Sample F, with a low Al content and an alloy composition close to Ti$_4$AlN$_3$, shows Ti$_2$AlN at 1000 °C and a shift of c-(Ti$_{0.72}$Al$_{0.28}$)N$_{0.58}$ peaks towards c-TiN position by Al depletion. Further annealing results in w-AlN and Al$_3$Ti formation. Similar to sample C, Ti$_2$AlN and Ti$_4$AlN$_3$ coexist between 1200 – 1400 °C. However, in this case only small quantities are
observed. At 1400 °C, c-TiN is the majority phase coexisting with small additions of Ti₄AlN₃, Al₃Ti, and w-AlN.

A similar phase transformation path is seen in all samples (Table 2) except for sample A, in which no Ti₄AlN₃ and Al₃Ti phases were detected. Formation of c-TiN, w-AlN, Al₃Ti, and Ti₂AlN always occurred below 1200 °C and Al₅Ti₂ appeared as precursor for Al₃Ti. The formation temperature of Ti₂AlN depends on the initial composition of the alloy (Ti₁₋ₓAlₓ)Nₓ but is below 1000 °C for all samples in this study. The end amount of c-TiN and w-AlN is affected by the initial metallic ratio of the coating, x, where more Al results in larger amounts of w-AlN, while Al₃Ti and Ti₂AlN become more dominant when reducing the nitrogen content. Coexistence of Ti₂AlN and Ti₄AlN₃ occurred in a temperature range between 1200 and 1400 °C, for alloy composition x < 0.63, with a strong correlation between the amount of Ti₂AlN at 1200 °C and the amount of Ti₄AlN₃ at 1400 °C. Additionally, an intermediate phase appeared in the same temperature range, which was only resolved when the MAX phase fraction was high.

3.3 Transformation of Ti₂AlN to Ti₄AlN₃

To elucidate the origin of the coexistence of Ti₂AlN and Ti₄AlN₃ local studies of the microstructure and chemical composition were conducted by STEM-in-SEM, TEM, and APT. This was done on sample C, which presented the largest amount of MAX phases in this temperature range.

Bright field STEM-in-SEM micrographs of sample C, annealed at 1200, 1300, and 1400 °C are shown in Fig. 4. MAX phase plates are seen in all samples. The plates are oriented arbitrarily with respect to the growth direction of the coatings and surrounded by secondary phases: w-AlN, Al₃Ti, and c-TiN. The MAX plates display a layered contrast, which is less
pronounced when the annealing temperature is increased. At 1400 °C, TEM and SAED (Fig. 5) reveal well-defined micrometer-sized Ti₄AlN₃ single crystal plates.

The layer contrast in the MAX plates was investigated further by APT and shown in Fig. 6. In the left column in Fig. 6 (a – c), slices (10 nm thick) of the reconstructed APT tips are shown. For clarity, only aluminum and nitrogen ions are presented. Arrows drawn inside the tips indicate the location and direction of 1D composition profiles presented in the right column, Fig. 6 (d – f). Based on the composition, the different regions in the 1D profiles were labeled with the corresponding phases. As a reference, the nominal stoichiometric composition of the MAX phases of interest are listed in Table 3.

Annealing sample C at 1200 and 1300 °C (Fig. 6) results in layers in the MAX plate that corresponds to chemical fluctuations of Al and N, while Ti presents a nearly constant concentration around 52 at. %. Based on the Al to N ratio, three main compositions are identified: Ti₂AlN, Ti₄AlN₃, and an intermediate phase. Ti to Al ratio for Ti₂AlN and Ti₄AlN₃ showed stoichiometric values of 2.00 ± 0.03 and 4.00 ± 0.02, respectively, while a nitrogen deficiency was observed which decreased with annealing temperature from δ = 0.20 to 0.04 for Ti₂AlN₁₋δ and from δ = 0.35 to 0.22 for Ti₄AlN₃₋δ. Substoichiometry is expected and can be accommodated in MAX phases [3,32,33]. The intermediate phase displays a composition of Al and N between Ti₂AlN and Ti₄AlN₃ and it is similar in composition to the MAX phase Ti₃AlN₂. Moreover at 1400 °C, the internal layering has almost disappeared and only Ti₄AlN₃ is left with some slight compositional variation corresponding to reminiscence of the layers.

3.4 Identification of intergrown structure Ti₆Al₂N₄

The intermediate phase observed in Fig. 3 and 6 is an intergrown structure of the two MAX phases Ti₂AlN and Ti₄AlN₃. High resolution STEM and more detailed XRD of sample C after annealing at 1300 °C are shown in Fig. 7. The recorded low angle x-ray diffraction peaks are
listed in Table 4. Figure 7 (b) shows a high resolution z-contrast micrograph of a MAX phase plate. A varying basal plane stacking sequence is observed. The bright layers display titanium atom columns and the dark layers aluminum.

The X-ray peaks in Fig. 7 (a) are inconsistent with the hypothetical metastable Ti$_3$AlN$_2$ MAX phase [16], since we observe peaks at 20 = 4.62 and 14.22°, which would correspond to the forbidden 0001 and 0003 peaks of any M$_3$AX$_2$ structure. Instead, these peaks originate from an intergrown structure, Ti$_6$Al$_2$N$_4$, which has the same chemical composition as Ti$_3$AlN$_2$ but a different crystal structure. The unit cell of Ti$_6$Al$_2$N$_4$ can be described as a half unit cell of Ti$_2$AlN and a half unit cell of Ti$_4$AlN$_3$ repeated three times, and c lattice parameter of 56.2 Å which is the sum of the c lattice parameters of Ti$_2$AlN and Ti$_4$AlN$_3$, multiplied by 1.5. Even though the symmetry of the P6$_3$/mmc space group to which regular MAX phases belong is broken, the intergrown structure belongs to the MAX phase family because of its hexagonal lattice and layered structure [34].

Figure 7 (b) shows different stacking sequences of half unit cell layers of Ti$_4$AlN$_3$ and Ti$_2$AlN. The different structures have different sequences: the combination of two Ti layers between Al layers corresponds to Ti$_2$AlN, the sequence of four Ti layers between Al layers corresponds to Ti$_4$AlN$_3$ and a mix of both corresponds to Ti$_6$Al$_2$N$_4$. Three Ti layers between Al layers were not found, which is also consistent with the XRD observations. We also note that when Ti$_2$AlN, Ti$_4$AlN$_3$, and Ti$_6$Al$_2$N$_4$ coexist, it occurs within the same grain. Pure crystallites of Ti$_4$AlN$_3$ were found only at 1400 °C.
4. Discussion

4.1 As-deposited state

Single-phase $c$-(Ti$_{1-x}$Al$_x$)N$_y$ thin films with B1 structure and composition values $y = 0.40$ to $0.58$ and $x < 0.55$ were grown by cathodic arc deposition. Alloys with $x \geq 0.55$ also contained w-AlN. (Ti$_{1-x}$Al$_x$)N$_y$ system is known to accommodate high N deficiencies via formation of nitrogen vacancies in the B1 structure, at least in the range $0.37 \leq y \leq 1.0$ [28,29,35]. The asymmetric miscibility gap of the TiN-AlN pseudo-binary phase diagram with its maximum located at high Al content, $x \approx 0.63$, provides a stronger driving force for segregation for the Al rich samples [36,37]. In this case, it is sufficient to cause AlN segregation during growth that results in a two phase microstructure consisting of $c$-(Ti$_{1-x}$Al$_x$)N$_y$ and w-AlN(Ti), i.e. samples A and B in this study. Similarly, there is a driving force for precipitation of metallic Al and Al-Ti mixtures in highly nitrogen deficient $c$-(Ti$_{1-x}$Al$_x$)N$_y$ solid solutions [31], which is seen to occur in samples B to F at elevated temperatures by the formation of Al$_5$Ti$_2$.

4.2 High temperature reactions

A general model of the solid state reaction path is suggested based on the XRD data recorded after annealing between 1000 °C and 1400 °C. The phase evolution with increasing annealing temperature can be summarized as follows:

1. Solid solution $c$-(Ti$_{1-x}$Al$_x$)N$_y$ becomes Al depleted and formation of the intermetallic Al$_5$Ti$_2$ takes place. Similar observations were made by annealing Ti/AlN [11,38,39] and Al/TiN multilayers [40], where the fast diffusion of N compared to Ti and Al and the preferential diffusion of N towards Ti lead to Al$_3$Ti formation. In this system, an intermediate intermetallic phase, Al$_5$Ti$_2$, is formed that transforms to Al$_5$Ti at higher temperatures.
(2) $\text{Al}_3\text{Ti}_2$ transforms to $\text{Al}_3\text{Ti}$ and the decreasing amount of $c-(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ evolves toward $c$-$\text{TiN}$ accompanied by the formation of nitrogen deficient $\text{Ti}_2\text{AlN}$ and $w$-$\text{AlN}$. The increase in annealing temperature enhances the species mobility which promotes formation of more complex unit cells like MAX phases [3,41]. Imanaka et al. showed that the activation energy of $\text{Ti}_2\text{AlN}$ growth is similar to the nitrogen diffusion in Ti [42], which confirms that nitrogen mobility and local chemical concentration control the phase formation [11,12,41–43]. Besides the diffusivity of the species, $c-(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$ likely acts as a precursor for $\text{Ti}_2\text{AlN}$ formation [20,41] due to similarities in the shared edges between $\text{M}_6\text{X}$ octahedral in MAX phases and the ones in the B1 structure of MX binaries [1,44]. $w$-$\text{AlN}$ formation is common as a competing phase in transition metal nitrides containing Al [44].

(3) $\text{Ti}_2\text{AlN}$ transforms into $\text{Ti}_4\text{AlN}_3$, with the presence of $\text{Ti}_6\text{Al}_2\text{N}_4$ during transformation, $\text{Al}_3\text{Ti}$ fraction increases while $c$-$\text{TiN}$ decreases, and $w$-$\text{AlN}$ remains stable. Diffusion of Al from $\text{Ti}_2\text{AlN}$ at high temperatures favors $\text{Ti}_4\text{AlN}_3$ formation and leads to the appearance of the intergrown structure $\text{Ti}_6\text{Al}_2\text{N}_4$. Annealing temperatures used in this study are above the melting point of $\text{Al}_3\text{Ti}$, ~ 1375 °C [45]. Melting of $\text{Al}_3\text{Ti}$ enhances the diffusion rate of the species similar to what has been observed by Lee et al. in the Ti-Al-N system [46] and by Kisi et al. in the Ti-Al-C system [47]. The result is an accelerated formation of $\text{Ti}_4\text{AlN}_3$. Moreover, $w$-$\text{AlN}$ is a stable phase that is not likely to take part in the reaction once formed [44].

As an example, we propose a reaction path for sample C based on X-ray diffractograms and atom probe data. Compositions were taken from APT measurements which cannot be assumed to be representative for the entire sample. Therefore, the reaction path is of qualitative nature and meant to give an idea of how the phases interact at different stages of the reaction.
The formation of small quantities of $\text{Al}_2\text{O}_3$ at high temperatures was observed in most of the samples. The presence of oxygen below 0.6 at. %, in as-deposited state cannot fully explain the presence of $\text{Al}_2\text{O}_3$. Instead we attribute the additional $\text{Al}_2\text{O}_3$ to residual $\text{O}_2$ and $\text{H}_2\text{O}$ in the DSC chamber / argon not captured by the zirconium trap used during all annealing treatments.

Sample A does not follow the suggested transformation path, due to the decomposition of $\text{Ti}_2\text{AlN}$ into $c$-$\text{TiN}$ and $w$-$\text{AlN}$ above 1000 °C. We suggest that the large amount of $w$-$\text{AlN(Ti)}$ present in the as-deposited state is responsible for the absence of $\text{Al}_3\text{Ti}$ and the instability of $\text{Ti}_2\text{AlN}$ at high temperatures. Beckers et al. showed that reactively sputtered $\text{Ti}_2\text{AlN}$ thin films decomposed already at ~800 °C by the out diffusion of Al and the formation of $c$-$\text{TiN}_x$ by $\text{Ti}_2\text{N}$ detwinning [48].

### 4.3 Formation mechanism of $\text{Ti}_4\text{AlN}_3$

The progression of chemically modulated layers inside the MAX plates at different temperatures suggests a thermally activated diffusion mechanism, where nitrogen layers replace Al layers in the $\text{Ti}_2\text{AlN}$ crystal. During the phase transformation an intergrown structure, $\text{Ti}_6\text{Al}_2\text{N}_4$, forms as a consequence of a specific stacking of $\text{Ti}_4\text{AlN}_3$ and $\text{Ti}_2\text{AlN}$ units.

The $\text{Ti}_4\text{AlN}_3$ formation mechanism proposed here is based on a transformation from a MAX phase of a low $n$ order to a higher order via deintercalation of the Al layers along the basal planes with concurrent introduction of N layers and detwinning. Two schematics describing the proposed mechanism are shown in Fig. 8 and Fig. 9.
The atomistic model in Fig. 8 describes several sequential steps of the formation of Ti$_4$AlN$_3$ from Ti$_2$AlN:

1. Intercalation of basal plane Al layers for N layers and detwinning.
3. Further intercalation of Al layers for N layers and detwinning until the entire crystal is Ti$_4$AlN$_3$.

The deintercalation process in the Ti$_2$AlN crystals is highly likely to trap some layers of Ti$_2$AlN inside the Ti$_4$AlN$_3$ crystals after the transformation is completed, which explains the remaining chemical fluctuation in Ti$_4$AlN$_3$ even after being heated to 1400 °C.

For a direct correlation with the experimental observations, our transformation model is schematically illustrated at a larger scale in Fig. 9. It shows the microstructure evolution during the transformation:

1. Starting material is a Ti$_2$AlN plate.
2. Intercalation of Al layers for N layers along basal plane leads to the formation of Ti$_4$AlN$_3$ layers and Ti$_6$Al$_2$N$_4$ layers inside the Ti$_2$AlN crystal. They are visible as nm-scale layers inside the grains (see Fig. 4).
3. Progressing intercalation during temperature increase. Ti$_4$AlN$_3$ and Ti$_6$Al$_2$N$_4$ layers become more dominant and frequent.
4. Ti$_4$AlN$_3$ dominates completely and the entire plate is now transformed.

MAX phase formation via a periodic intercalation of the A-element into a M$_{1-n}$X$_n$ preordered matrix is a mechanism proposed by Zhou et al. [49] and presented later by Riley et al. as a low temperature solid state synthesis method for MAX phase formation in bulk materials [50,51]. The suggested mechanism starts with a binary precursor, M$_{1-n}$X$_n$, in which a sequence
of vacancy ordering, twinning, and intercalation of A-element leads to the formation of a MAX phase. Intercalation is a reversible mechanism and is thermally activated [49,52]. MAX phase formation via intercalation has been reported in different ternary systems, e.g. Ti$_3$SiC$_2$, Ti$_2$AlC, Ti$_3$AlC$_2$ [13,53,54]. It is important to note that the precursor used is a binary phase rich in X-element vacancies, and intercalation has only been shown in systems with carbon as the X element.

The presented results extend the mechanism of intercalation to a ternary phase, where the precursor is a MAX phase of a low $n$ order, i.e. Ti$_2$AlN. By de-intercalation of Al layers concurrently with introduction of N layers and detwinning, a MAX phase of higher $n$ order is formed, i.e. Ti$_4$AlN$_3$. Similar observations have been done in other transition metal carbide systems, where a full or a partial transformation was observed by annealing thin films or bulk material. In the Ti-Al-C system, Kisi et al. [47] and Wu et al. [55] showed a full conversion of Ti$_2$AlC into Ti$_3$AlC$_2$, while in the same system Lane et al. [56–58] and Zhang et al. [59] presented the intergrown phase Ti$_5$Al$_2$C$_3$ in coexistence with Ti$_3$AlC$_2$ by annealing Ti$_2$AlC. In all these cases, the temperatures used were above 1400 °C with annealing times between 1 to 8 hours. Further, in the systems Ti-Si-C and Ti-Ge-C, presence of intergrown phases were observed to coexist with their related MAX phases, i.e. Ti$_7$Si$_2$C$_5$ with Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ by Palmquist et al. [34], and Ti$_7$Si$_2$C$_5$ and Ti$_5$Si$_5$C$_3$ with Ti$_2$SiC, Ti$_3$SiC$_2$ and Ti$_4$SiC$_3$ by Högb erg et al. [60]. Scabarozi et al. [61] demonstrated that Ti$_7$Si$_2$C$_5$ can be synthesized as a phase pure epitaxial thin film. In ternary systems containing nitrogen, Lee et al. were able to obtain full transformation of Ti$_2$AlN into Ti$_4$AlN$_3$ by annealing a powder mixture at 1300 °C for 20 days, which at the time (1997) was wrongly believed to be Ti$_3$Al$_2$N$_2$ [46]. In our study, we were able to obtain full transformation of Ti$_2$AlN into Ti$_4$AlN$_3$ by annealing up to 1400 °C with no dwell time.
In order for this transformation to take place, several conditions must be fulfilled: (1) the ternary system M-A-X must have at least two $M_{1+n}AX_n$ phases thermodynamically stable, (2) the MAX phase to be transformed into a higher $n$ order must be stable at the temperature where the transformation takes place, and (3) high annealing temperature must be applied, i.e. above 900 °C. Moreover, transformation occurs from a low $n$ order MAX phase to the next thermodynamic stable MAX phase with higher $n$ order. The full transformation takes place if sufficient amount of X element and energy is supplied to the system, and it can be accelerated by the melt of an A-rich phase [46,47].

We suggest that with the transformation mechanism we propose, it is possible to obtain MAX phases of high $n$ order in thin films which has not been obtained previously by direct nucleation and growth, like Ti$_4$GaC$_3$, Nb$_4$AlC$_3$ and V$_4$AlC$_3$.

5. Conclusions

Formation of MAX phase Ti$_4$AlN$_3$ in flake-like powder was possible via solid state reactions in a nitrogen deficient cubic solid solution $(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y$. The as-deposited composition where Ti$_4$AlN$_3$ was obtained ranged from $x = 0.28$ to 0.55 and $y = 0.40$ to 0.58. Phases like Ti$_2$AlN, w-AlN, c-AlN, Al$_5$Ti$_2$, and Al$_3$Ti were present and their quantity varied with the as-deposited composition of the thin film, as was the case for Ti$_4$AlN$_3$ too.

We have showed that formation of Ti$_4$AlN$_3$ takes place inside the preformed MAX phase Ti$_2$AlN single crystal plates by a thermal activated diffusion process. The mechanism of transformation suggested is the intercalation of Al layers for N layers along the basal plane of the Ti$_2$AlN crystals, leading to the formation of a MAX phase of higher $n$ order, Ti$_4$AlN$_3$. Therefore, a prerequisite for obtaining large quantities of Ti$_4$AlN$_3$ is the formation and stability of Ti$_2$AlN above 1200 °C. During the transformation from Ti$_2$AlN to Ti$_4$AlN$_3$, an intermediate Ti$_6$Al$_2$N$_4$ phase was observed and characterized to be an intergrown structure.
whose unit cell consists of Ti$_2$AlN and Ti$_4$AlN$_3$ half unit cells. This phase confirms intercalation as the formation mechanism of Ti$_4$AlN$_3$.

6. Acknowledgments

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7. References


[34] J.P. Palmquist, S. Li, P.O.Å. Persson, J. Emmerlich, O. Wilhelmsson, H. Högborg, et


Table captions

Table 1. Pearson coefficient of aluminum, titanium and nitrogen for as-deposited sample A, C and F. * Data from samples grown under similar conditions taken from Schramm et al. [28] for comparison. Value of 0 indicates random distribution and 1 complete segregation of the element.

Table 2. Phase identification by X-ray diffraction after annealing at different temperatures.

Table 3. Nominal stoichiometric composition of the possible MAX phases in the Ti-Al-N system.

Table 4. X-ray powder diffraction data collected and shown in Fig. 7 (a).
Figure captions

Figure 1. Ternary composition map showing with dots the total alloy composition and their labeling from A to F. The position for the Ti$_2$AlN and Ti$_4$AlN$_3$ MAX phases are marked with stars. Horizontal lines represent fixed nitrogen contents given in the notation (Ti$_{1-x}$Al$_x$)$_y$N.

Figure 2. X-Ray powder diffractograms of as-deposited (Ti$_{1-x}$Al$_x$)$_y$N$_y$ coatings. The aluminum content ranges from $x = 0.28$ to 0.63 and nitrogen fraction from $y = 0.40$ to 0.58. The total 2θ range measured is 5° to 85°.

Figure 3. X-ray powder diffractograms recorded after annealing at 1000 °C – 1400 °C for (a) (Ti$_{0.27}$Al$_{0.63}$)$_{0.46}$N$_{0.46}$, (b) (Ti$_{0.52}$Al$_{0.48}$)$_{0.40}$N$_{0.40}$, and (c) (Ti$_{0.72}$Al$_{0.28}$)$_{0.58}$N$_{0.58}$.

Figure 4. Bright field STEM-in-SEM micrographs of sample C at different post annealing states: (a) 1200 °C, (b) 1300 °C, and (c) 1400 °C. MAX phase plates and secondary phases are labeled for guidance.

Figure 5. (a) TEM micrograph of sample C post annealing at 1400 °C. Circumference of the MAX plate is marked by dashed line. (b) Selected area diffraction pattern from a Ti$_4$AlN$_3$ crystal.

Figure 6. Left column (a – c): 10 nm thick slices of reconstructed 3D atom probe tips of sample C after annealing at 1200 °C, 1300 °C and 1400 °C, respectively. Only Al and N ions
are presented for clarity. Right column (d – f): 1D concentration profiles extracted from the corresponding APT reconstructions, exact location is highlighted with arrows. The different composition regions in the 1D profiles are labeled with the corresponding phases. Line curvature in (b) is a reconstruction artifact. Key: 211 – Ti$_2$AlN; 413 – Ti$_4$AlN$_3$; IntP – Intermediate phase.

Figure 7. (a) Low angle x-ray diffractogram of sample C annealed at 1300 °C. (b) High resolution z-contrast STEM image displaying the coexistence of Ti$_2$AlN, Ti$_4$AlN$_3$, and Ti$_6$Al$_2$N$_4$ along [1-210] direction. Labels indicate the number of adjacent N-rich basal planes.

Figure 8. Atomic scale model of the transformation mechanism from Ti$_2$AlN to Ti$_4$AlN$_3$ via intercalation and detwinning.

Figure 9. Large scale view of the transformation mechanism of Ti$_2$AlN into Ti$_4$AlN$_3$. 
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<th>Sample</th>
<th>Label</th>
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<td></td>
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<td>C</td>
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<td>(Ti_{0.37}Al_{0.63})N_{0.46}</td>
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### Phases present at room temperature after annealing (no dwell time)

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<th>Sample</th>
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<th>1300 °C</th>
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<td>211; TiAIN; TiN; AlN</td>
<td>TiAIN; TiN; AlN</td>
<td>TiN; AlN</td>
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<tr>
<td><strong>B</strong></td>
<td>211; Al$<em>{3/2}$Ti$</em>{1/2}$ TiAIN; TiN; AlN</td>
<td>211; Al$<em>{3/2}$Ti$</em>{1/2}$ TiAIN; TiN; AlN; Al$_2$O$_3$</td>
<td>211; 413; IntP; Al$<em>{3/2}$Ti$</em>{1/2}$ TiN; AlN; Al$_2$O$_3$</td>
<td>413; Al$<em>{3/2}$Ti$</em>{1/2}$ TiN; AlN; Al$_2$O$_3$</td>
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<td><strong>C</strong></td>
<td>Al$<em>{3/2}$Ti$</em>{1/2}$ TiAIN; TiN; AlN</td>
<td>211; IntP; Al$<em>{3/2}$Ti$</em>{1/2}$ TiN; TiN; AlN; Al$_2$O$_3$</td>
<td>211; 413; IntP; Al$<em>{3/2}$Ti$</em>{1/2}$ TiN; TiN; AlN; Al$_2$O$_3$</td>
<td>413; Al$<em>{3/2}$Ti$</em>{1/2}$ TiN; AlN; Al$_2$O$_3$</td>
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<td><strong>D</strong></td>
<td>211; Al$<em>{3/2}$Ti$</em>{1/2}$ TiAIN; TiN; AlN</td>
<td>211; IntP; Al$<em>{3/2}$Ti$</em>{1/2}$ TiN; TiN; AlN; Al$_2$O$_3$</td>
<td>211; 413; IntP; Al$<em>{3/2}$Ti$</em>{1/2}$ TiN; TiN; AlN; Al$_2$O$_3$</td>
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<td></td>
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<td><strong>F</strong></td>
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**Key:**
- TiAIN – c-(Ti$_{1-x}$Al$_x$)N$_y$
- TiN – c-TiN
- AlN – w-AlN
- 211 – Ti$_2$AlN
- 413 – Ti$_2$AlN$_3$
- IntP – Intermediate phase
<table>
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<td>Aluminum (at. %)</td>
<td>Nitrogen (at. %)</td>
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<td>2θ measured</td>
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<td>hkl</td>
<td>Phase</td>
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</table>
(a) Sample A

(b) Sample C

(c) Sample F

\[ \begin{align*}
\text{Ti}_3\text{AlN}_x & \quad \text{Al}_3\text{Ti} \\
\text{Ti}_2\text{AlN} & \quad \text{Al}_4\text{Ti}_3 \\
\text{Int. phase} & \quad \text{Al}_2\text{O}_3 \\
\text{w-AlN} & \quad \text{c-TiN}
\end{align*} \]
3D reconstructions

(a) $T = 1200 \, ^\circ\text{C}$

(b) $T = 1300 \, ^\circ\text{C}$

(c) $T = 1400 \, ^\circ\text{C}$

1D composition profiles

(d) Ti

(e) Ti

(f) Ti

Composition (at. %)

Distance (nm)
(a) \( \text{Ti}_4\text{AlN}_3 \), \( \text{Ti}_2\text{AlN} \), \( \text{Ti}_5\text{Al}_{2}\text{N}_4 \) 

Sample C 
\( T = 1300 \, ^\circ\text{C} \)

(b) 
\begin{align*}
\text{Al} & \quad \text{Ti}_2\text{AlN} \\
\text{Ti} & \quad 2 \quad 2 \quad 2 \\
\text{Ti}_5\text{AlN}_3 & \quad 4 \quad 4 \\
\text{Ti}_2\text{Al}_2\text{N}_4 & \quad 2 \quad 2 \quad 2 \quad 4 \quad 4 \quad 2 \quad 2 \\
\end{align*}

\( \varepsilon \)-axis 

5 nm
1. Ti$_2$AlN
2. Intergrown structure Ti$_{6}$Al$_{2}$N$_{4}$
3. Ti$_4$AlN$_3$
A.

1. Ti$_2$AlN plate

2. Ti$_6$Al$_2$N$_4$

3. Ti$_4$AlN$_3$

4. Ti$_4$AlN$_3$ plate

↑ c-axis ↔ basal plane

Increase temperature