# PREPARATION AND STUDY OF NANOSTRUCTURED TIALSIN THIN FILMS

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## ABSTRACT

*TiAlSiN thin film coatings were deposited by DC reactive magnetron sputtering of TiAlSi target with 40 at.% Ti, 40 at.% Al and 20 at.% Si, performed in $N_2$-Ar gas mixture. The sputtering power used in these experiments was controlled for 400 W. The bias voltage of the substrates was kept at -20 V DC and the temperature at 500 $^0$C. All the samples were prepared with a constant flow rate of Ar and different nitrogen flow rates, which were selected from 1.25 sccm to 4.0 sccm. Nanostructured TiAlSiN coatings were developed on Si(100) and HSS substrates. Microstructure investigation of the coatings was performed by transmission electron microscopy investigation, structure investigation was performed by XRD analysis, and the mechanical properties of the coatings have been tested by ball-on-disk tribological investigation and micro-Vickers hardness measurements. In this paper will be shown that for optimized nitrogen concentration the microstructure of TiAlSiN coating evolve from a competitive columnar growth to a dendritic growth one with very fine nano-lamellae like morphology. The developed nanostructured TiAlSiN coatings have hardness HV exceeding 40 GPa and show an increased abrasive wear resistance.*

**Keywords**: thin film, sputtering, microstructure, mechanical properties

### 1. Introduction

Preparing multiphase nanostructured materials in the form of thin film coatings and understanding the growth mechanism of the developing film is a challenge for material scientists, as these materials have very special physical, tribomechanical and structural properties.

These materials have very high hardness, sometimes exceeding 40-60 GPa, high elasticity, up to 80% recovery energy, and high thermal stability, which was observed at temperatures as high as 1100 $^0$C.

The nanocomposite nc-TiAlN/a-$Si_3N_4$ system is an outstanding material with these exceptional properties, which could come from the phase segregation of strongly immiscible components observed for nanocrystals of TiAlN embedded in an amorphous $Si_3N_4$ matrix phase [1].

Our experiments aimed to obtain a structure which has these properties.

### 2. Experimental details

We used the DC excited unbalanced magnetron sputtering method to build up thin films with TiAlSiN composition. The reactive sputtering of TiAlSi target with 40 at.% Ti, 40 at.% Al and 20 at.% Si was performed in $N_2$-Ar gas mixture. The details of the experimental sputtering system were reported elsewhere [2]. The overall purity of this target is 99.6% guaranteed.

Prior to the experiments the vacuum chamber was evacuated with a turbomolecular pump to a base pressure of ~ $2 \cdot 10^{-6}$ Torr. The working pressure of $3 \cdot 10^{-3}$ Torr was obtained with an Ar+N mixture, the Ar gas throughput was controlled by a servo valve controller (MFC-Granville Phillips S 216), and measured by a GFM 17 Aalborg mass flow meter. The $N_2$ throughput was controlled by a digital mass flow controller (Aalborg DFC 26).

The substrates for the films were high speed steel (HSS) for tribological testing and <100> Si wafer for structural characterization. Their distance and position relative to the target surface was 110 mm horizontally, and centered vertically, and was kept constant throughout the experiment series.

The substrates were positioned statically in a heated Mo boat which allowed also the application of the bias voltage. For temperature measurements a K-type chromel-alumel thermocouple was positioned on the substrate holder.

Before the deposition process was started, the

chamber was filled to 0.8 Pa with Ar, in order to plasma-etch the substrate surface for 10 minutes. The etching voltage was limited up to 350 V. During this process the target was also pre-sputtered, behind a closed shutter, with a sputtering power of 200 W.

The sputtering power used in these experiments was 400 W. The bias voltage was kept at -20 V DC and the temperature of the samples at 500 $^0$C. All the samples were prepared with a constant flow rate of Ar, namely 6.0 sccm. The preparation parameters are summarized in Table 1.

**Table 1. Summary of deposition parameters**

| Sample | $q_{N2}$ (sccm) | $a_D$ (Å/s) | d (kÅ) | $p_d$ (mTorr) |
|---|---|---|---|---|
| M18 | 1.25 | 4.7 | 20.2 | 2.9 |
| M17 | 1.50 | 4.4 | 20.2 | 3.3 |
| M16 | 2.00 | 4,3 | 20. 1 | 3.0 |
| M19 | 2.50 | 4.3 | 20.1 | 3.0 |
| M20 | 3.00 | 3.8 | 20.2 | 3.0 |
| M21 | 3.50 | 3.4 | 20.0 | 3.0 |
| M22 | 4.00 | 3.2 | 20.0 | 2.9 |

The microstructures of as-deposited coatings were studied in a JEOL 100U transmission electron microscope at Sapientia University, after they were prepared for electron transparency by cross section ion milling in a Technoorg Linda IV/H/L unit. The high energy thinning process was followed by a low energy (200 eV) etching, for removal of amorphous artifacts. Bright Field (BF) and Dark Field (DF) imaging techniques were used to investigate crystalline structure, and SAED (Selected Area Electron Diffraction) patterns were recorded to identify the crystallographic orientations of the found phases.

### 3. Microstructure

In case of low nitrogen throughput in the process of preparation ($q_N$=1.5 sccm), the transmission electron microscopy (TEM) image clearly shows that by transition from the TiAlSi base layer to the TiAlSiN layer, we have a transition of microstructure from competitive columnar growth to a dendritic growth, as it can be seen on figure 1.

The analysis of the SAED pattern shown in figure 1 reveals the presence of the following phases: fcc-TiAlN, hex β-$Si_3N_4$ and $TiSi_2$, respectively.

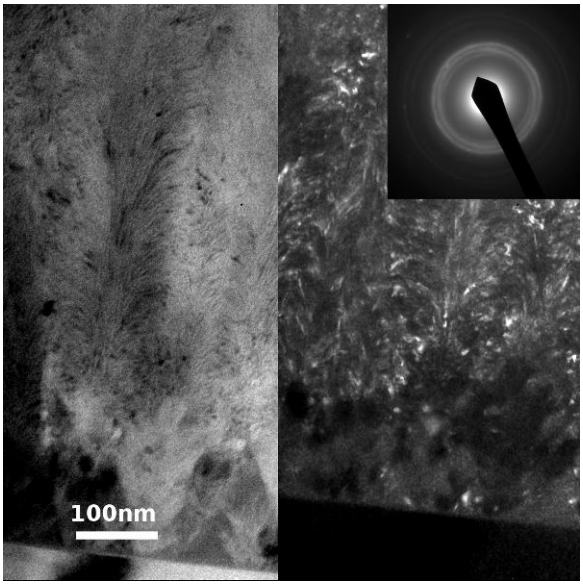


**Fig. 1 – TEM images BF and DF at 25k magnification and SAED pattern of sample M_17 prepared by $q_N$=1.5 sccm**

With a small increase in $N_2$ flow rate (2 sccm), and by growing the TiAlSiN layer without an interface layer of TiAlSi, as in the case of sample M_16, shown in figure 2, the bent lamellar structure caused by the transition layer is no longer observable, and the fine nano-lamellae in the growing film are perpendicular to the surface of the substrate, therefore in the direction of film growth.

The SAED inserts shows a clear (111) texture from the alternating layers of lamellae. The crystallite size in this case is very small, as it can be seen on DF image, right side of the image in Fig. 2.

Increasing further the N content as in the case of sample M_19, the morphology of the thin film shows no obvious change (Fig. 3), except for an appearance of the accumulation of some segregated phases at the column boundaries, which can be observed on figure 4.

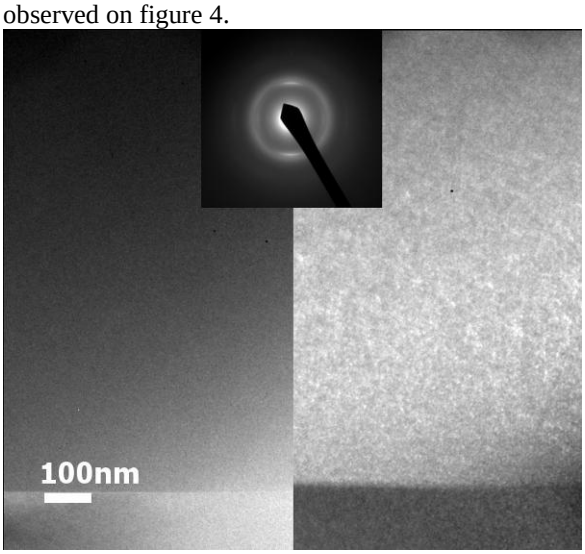


**Fig. 2 – TEM images BF and DF taken at 20k magnification and SAED pattern of sample M_16**

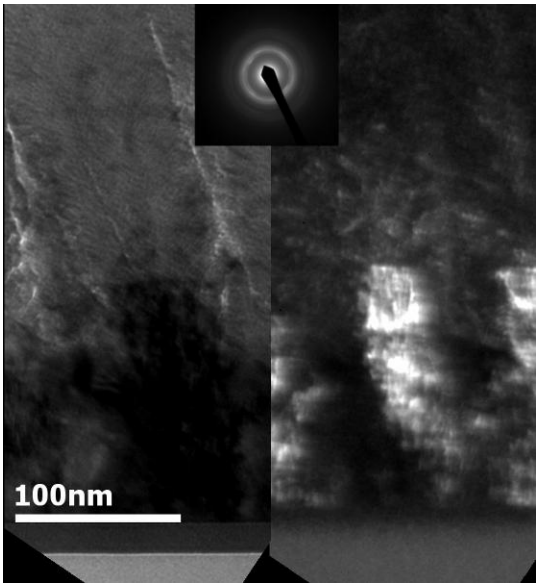


**Fig. 3 – TEM images BF and DF shown at 40k magnification, and SAED pattern of sample M_19**

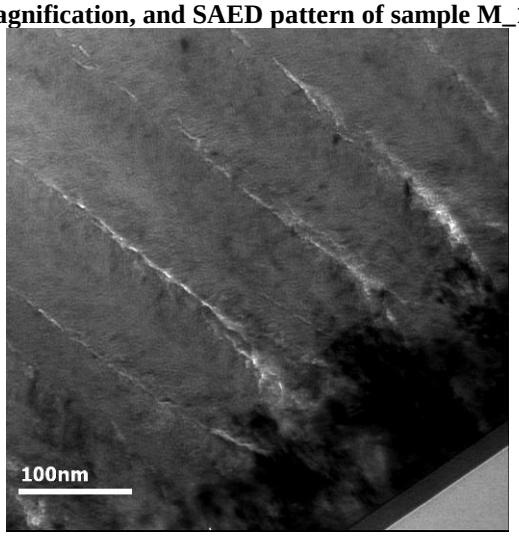


**Fig. 4 – Bright field TEM image at 40k magnification of sample M_19**

**4. Composition**

Following to the structural analysis performed in the JEOL 100U transmission electron microscope, some of the samples were taken to perform compositional analysis with the EDS (Energy Dispersive Spectroscopy) in a analytical transmission electron microscope Philips CM20 (200 keV). The elemental compositions of selected samples investigated by EDS analysis are presented in Table 2.

**Table 2. EDS compositional analysis results**

| Sample | M_17 | M_16 | M_19 |
|---|---|---|---|
| | | | |
| Ti (at%) | 21 | 19 | 12 |
| Al (at%) | 31 | 35 | 22 |
| Si (at%) | 14 | 14 | 19 |
| N (at%) | 20 | 31 | 47 |
| O (at%) | 1.5 | 1.8 | 3.2 |

The increase of nitrogen flow rate selected for various deposition processes clearly show the increase of nitrogen amount in the composition of the films.

**5. XRD analysis**

XRD measurements were conducted on a number of samples, following the Bragg-Brentano θ-2θ geometry, performed in a Philips PW 1710 diffractometer.

For evaluation of the obtained diffractograms (Fig. 5 – Fig. 7) we used the following standard markers, powder diffraction maxima:

- β–$Si_3N_4$ (PDF-33-1160), hexagonal;
- α–$Si_3N_4$ (PDF-41-0360), hexagonal;
- AlN (PDF 46-1200);
- TiN(PDF 38-1420);
- Al (PDF 04-0787);
- β-Ti (PDF 44-1288);
- α-Ti (PDF 44-1294);
- Si (PDF 27-1402).

We identified on the XRD patterns the crystalline phases by assigning the acquired spectra's peaks to the characteristic reflections from the reference spectra, and we determined the interplanar distances for each reflections.

In some of the spectra we had a very strong reflection peak at 2θ =39°, which origin is still unknown, this problem needs clarifying.

It is presumable, that the peak very close to the 200 peak is a response from the TiAlSi transition layer.

Based on the SAED analysis, the hexagonal $Ti_3Al$ phase has the strongest line (201) in this position, which is corresponding to an interplanar distance of 0.220 nm, and another strong peak is present at 0.232 nm (JCPDS 09-0098).

In the XRD spectra of the sample M_17 we can identify the d=2.4272 angstrom planar distance, which covers very well the reference line for the (111) planes of the TiN phase.

Furthermore, the presence of interplanar distance with d=1.4842 Å, which can be attributed to the (220) TiN reflection, we can't rule out the presence of the β-$Si_3N_4$, because the reference markers for this phase are in good accordance with the other peaks in the spectra. The peak appearing at 2θ=74° indicates a possibility, that the AlN phase is also present. The presence of this phase is interesting because it shows us, that the solubility of the aluminum is smaller at this composition.

In the case of the sample M_19 the two peaks specific for TiN reflections are strongly widened, which can be understand as the TiAlN crystallites in the film are very small. The form of the 2 peaks suggests that $Si_3N_4$ phase is present, also possible in a very small crystalline form.

In the XRD spectra of the sample M_21 we could identify clearly the peaks for TiN (111) and TiN (200), with d=2.4172 Å and d=1.4842 Å, respectively.

Summarizing the XRD results we can say that increasing the N content of the films the peaks widen and displace to the higher crystallographic constants.

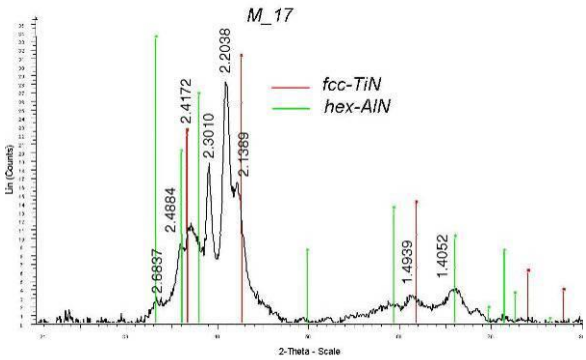


**Fig. 5 – XRD spectra of sample M_17**

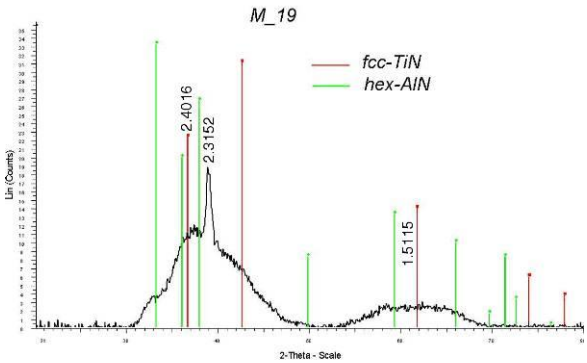


**Fig. 6 – XRD spectra of sample M_19**

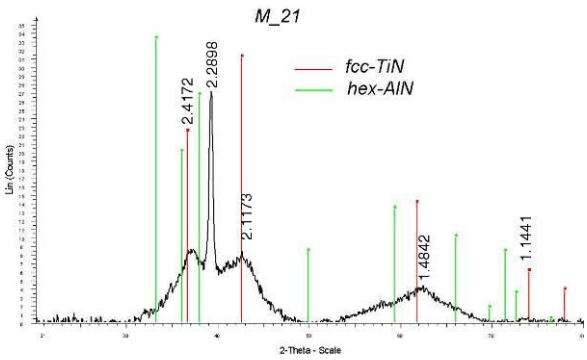


**Fig. 7 – XRD spectra of sample M_21**

## 6. Tribological measurements performed by Ball-on-Disk method

The tribological investigations were conducted on TiAlSiN films with thicknesses around 3 μm, deposited on HSS substrates. For testing the wear resistance of the coatings we performed ball-on-disk wear measurements by using a DTHT70010 High temperature tribometer of CSM Instruments.

In the abrasive wear experiments we used hard counter materials of 100Cr6 steel and $Si_3N_4$, balls with 6 mm diameter, and 4.8 mm diameter, respectively.

The selected samples for tribological investigations were M_16, M_19, M_22. The measured wear rates show that sample M_22 has the lowest wear rate, compared to other selected samples (Fig. 8).

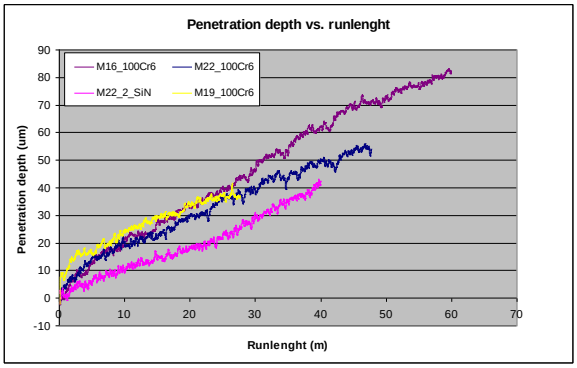


**Fig. 8 –Comparative graphs indicate the wear of the selected samples**

## 7. Microhardness measurements

For microhardness measurements we used a CV-400AAT type micro-Vickers instrument with diamond pyramid indenter. The coatings of TiAlSiN films deposited on Si and HSS substrates were both tested.

The results presented in Table 3 are average values of repeated measurements. Although the film's thickness was greater than 2 μm, in order to exclude the influence of the substrate effect, we performed the measurements with 10 g and 20 g loading force.

The indentation time was 30 s, with 10 s holding time. The hardness measurements results are presented in table 3 are expressed in HV number of $kgf/mm^2$.

**Table 3. Results of microhardness measurements**

| | Si10g | HSS10g | Si25g | HSS25g |
|---|---|---|---|---|
| M17 | 2267 | ---- | 1698 | 2027 |
| M16 | 1771 | 2081 | 1761 | 1704 |
| M19 | 2088 | 2408 | 1799 | 2167 |
| M20 | 2908 | 2796 | 2054 | 1641 |
| M22 | 3460 | 4011 | 2341 | 3185 |

We can observe how the increase in N concentration the hardness of the sample increases.

The 40 GPa hardness and the very low wear rate of the TiAlSiN film are important experimental results. One of the major requirements for superhard thin films according to the literature is, that the oxygen content should not be higher than 0.5 at % [1].

Our ongoing experiments are running nowadays for deposition of TiAlSiN thin films with reduced oxygen content, by using of UHV environment, and the concerning results will be published in a following paper.

## 8. Conclusions

TiAlSiN thin film coatings were deposited by DC reactive magnetron sputtering of TiAlSi target with 40 at. % Ti, 40 at. % Al and 20 at.% Si, performed in $N_2$-Ar gas mixture. The sputtering power used in these experiments was controlled for 400 W. The bias voltage of the substrates was kept at -20 V DC and the temperature at 500 $^0$C. All the samples were prepared with a constant flow rate of Ar, namely 6.0 sccm. Different nitrogen flow rates were used in preparation, which was selected from 1.25 sccm to 4.0 sccm. Nanostructured TiAlSiN coatings were developed on Si(100) and HSS substrates. Microstructure investigation of the coatings was performed by transmission electron microscopy investigation, structure investigation was performed by XRD analysis, and the mechanical properties of the coatings have been tested by ball-on-disk tribological investigation and micro-Vickers hardness measurements.

The following experimental results have been obtained:

a.) For optimized nitrogen concentration the microstructure of TiAlSiN coating evolve from a competitive columnar growth to a dendritic growth one with very fine nano-lamellae like morphology.

b.) We have studied the microstructure, composition and mechanical properties of these nanostructured coatings and established that superhard TiAlSiN coatings with hardness HV exceeding 40 GPa and high performance of mechanical properties with increased abrasive wear resistance can be obtained.

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