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SOME REMARKS ON THE TERNARY TiAlSiN THIN FILMS DEVELOPED UNDER SPECIFIC CONDITIONS

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Abstract: *The need for more performant wear resistant coatings shifted the attention from TiN to the extension of the material system with additional elements like Al and Si. This paper presents our findings in relation with this material system. We studied the evolution of the growth morphology in terms of nitrogen flow and temperature to track the changes which occur in the structure of the coatings. Our coatings exhibited a weak textured growth at the lowest nitrogen flows. This structure turned into a randomly oriented diffuse nanocrystalline one, and further increasing the nitrogen flow during the deposition the morphology of the coating changed again to a textured one. We found that the switching points for these transitions are dependent of temperature.*
Key words: *TiAlSiN, thin film coatings, reactive sputtering, XTEM investigation, growth morphology, texture evolution*

1. INTRODUCTION

In the field of processing thin film hard coatings, with the aim for improvement of mechanical properties, the overly successful titanium nitride [1, 2] material system has been used since many years. The need for even more performant wear resistant coatings shifted the attention from TiN to the extension of the material system. By adding other elements the properties of the coating can be improved. One of the directions of this venture is creating thin films by extending the system to four elements with addition of Al and Si [3-5]. According to the literature this material system, if created as a coating developed under specific circumstances with nanocomposite structure, can offer several advantages over the original material system [4, 5]. We found only partial information on the growth morphology of these coatings in the literature with regard to nitrogen content and temperature. The differences between the used apparatus and methods used, made it impossible to compare and synthesize these results into a clear morphology evolution scheme. We published some preliminary results [6], but we did not cover the issue as in that paper.

2. EXPERIMENTAL DETAILS

The sputtering system used in this experiment series is an unbalanced magnetron direct current system. The details about it were reported in [7]. Controlling the system parameters throughout of the deposition process is essential, so the sputter system also contains updates described in [8]. A special sample holder was designed and manufactured to strictly control the sample temperature. The holder is based on a 80µm thick molybdenum sheet, which is used as a resistive heater, and it features 4mm thick polished steel slabs for sample backing. These steel slabs are introduced in the sample holder system to increase the thermal inertia of the system, which is needed in order to maintain stable temperature. The heating power for 500°C sample temperature is around 22W. The heat capacity of the steel slabs is 6J/K, that of the molybdenum sheet is 3e-3J/K. Therefore with the steel slabs the temperature of the sample holder can be kept in control much easier via

automatic control. The temperature is measured with a K type thermocouple, and the signal is used as input for the temperature control unit designed in-house for this purpose.

For these experiments a composite Ti-Al-Si (40-40-20 at%) target was used, and the process gases were of high purity .

The deposition process consisted of the following steps:

- Plasma cleaning of the substrates for 300 seconds at -360V and 10-20 mA;
- Presputtering the target for cleaning with target shutters closed 60 seconds;
- Deposition of base layer of TiAlSi for 300 seconds;
- Deposition of TiAlSiN layer for 2 hours.

After the deposition process the samples were marked for identification.

For transmission electron microscopy cross section ion milled samples were prepared in a Technoorg Linda IV/H/H ion milling unit, the thinning was conducted at 10keV ion beam energy and it was completed by a 200eV cleaning process for the elimination of artifacts.

The microstructure and morphology of the as-deposited coatings were examined in a 100kV JEOL 100U electron microscope. Bright field and dark field photomicrographs were recorded via a 1Mpixel Gatan CCD camera and Selected Area Electron Diffraction patterns were also acquired from the top layer of the coatings. Some samples were also studied in a Phillips CM20 analytical TEM courtesy of Dr. Prof. Emeritus Barna Péter from RITPMS, Budapest.

3. SAMPLE SET

All the samples discussed in detail in this article were prepared with identical process parameters except the nitrogen mass flow introduced in the system, the nitrogen mass flows and corresponding nitrogen partial pressures are contained in Table 1.

Table 1

Nitrogen flow for samples

ID	q_{N_2}	Resulted N_2 partial pressure [Pa]
M099	2	0.0839
M100	3	0.121
M037	4	0.135
M062	6	0.184
M064	8	0.215
M066	9.3	0.229

The other determining parameters for the experiment series throughout the samples were as follows:

- Base pressure: 4e-4 [Pa];
- Sample temperature 400^0[C];
- Sample bias voltage -20[V];
- Deposition pressure 0.4 [Pa];
- Sputtering power 400 [W];
- Plasma cleaning at -360[V] @ 6.5 [Pa].

The sputtering process was started in pure Ar atmosphere, and the nitrogen flow was increased when necessary from 0 to the nominal value linearly during a 120 second period.

4. RESULTS AND DISCUSSION

4.1 BASE LAYER

In all samples a base layer of TiAlSi was deposited as a base layer for the nitride phase.

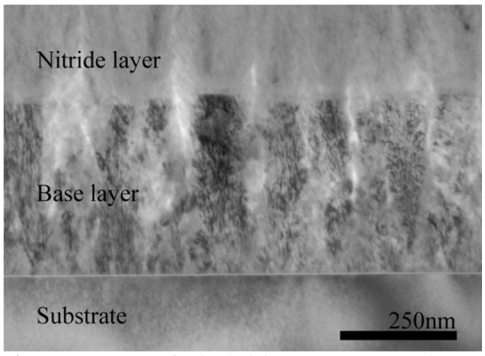

Fig. 1. Base layer of TiAlSi in center (sample M062)

This layer shows columnar growth morphology with a lamellar substructure perpendicular to the substrate (see figure 1.). The layer itself is microcrystalline with a texture.

The crystal structure is FCC aluminum as can be seen on the indexed monocrystalline diffraction pattern in figure 2. The reflections marked with white text are the normal FCC reflections from the aluminum lattice, the red marked ones are superlattice reflections, they arise from substitution of the Al atoms with Ti atoms in the crystal structure.

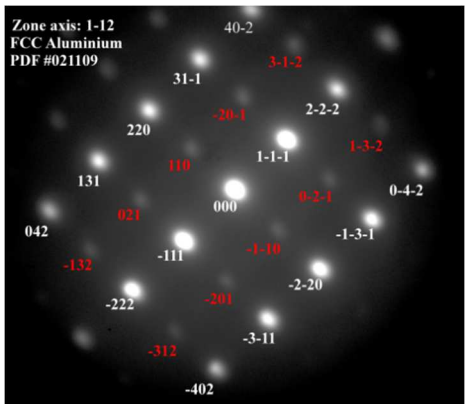

Fig. 2. Indexed diffraction pattern from a single column of the base layer

4.2 NITRIDE LAYERS

At the lowest nitrogen partial pressure, but with nitrogen present we can observe on the dark field image part of Figure 3. that the size of the crystalline grains is around 2 nm.

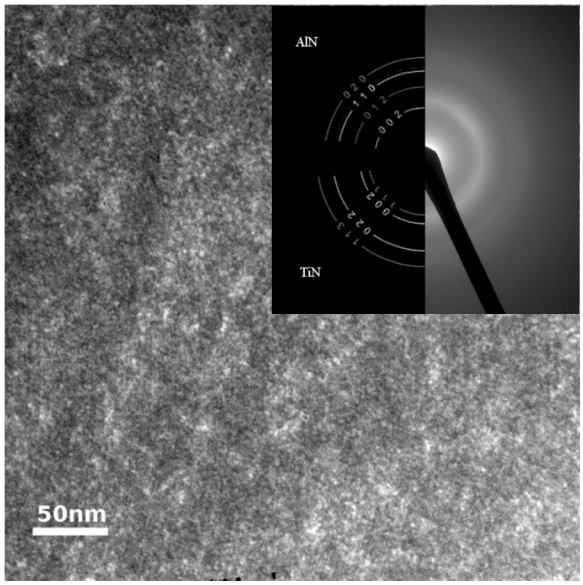

Fig. 3. Dark field microphotograph and SAED pattern (insert) of sample M099

These nanometric grains were identified via selected area electron diffraction as being hexagonal AlN and FCC TiN grains. The SAED pattern is diffuse; the circular symmetry of the pattern is not perfect, indicating the presence of a weak texture in this coating.

As we increase the nitrogen partial pressure (sample M100), the grain size in the coating further decreases, and in this case we cannot observe any directionality in the SAED pattern in Figure 4, thus the grains forming this pattern are randomly oriented. These grains are identifiable as FCC TiN grains. The literature available suggests that this structure, notably nanometric size TiN grains embedded in a Si_3N_4 matrix provide the coating extraordinary mechanical properties [9, 10]. We have tested this coating via Vickers microhardness at a load of 10mN and from 9 averaged measurements obtained a value much lower than expected based on the literature, notably 1700HV. The exact measurement method for the indentations is described in detail in [11].

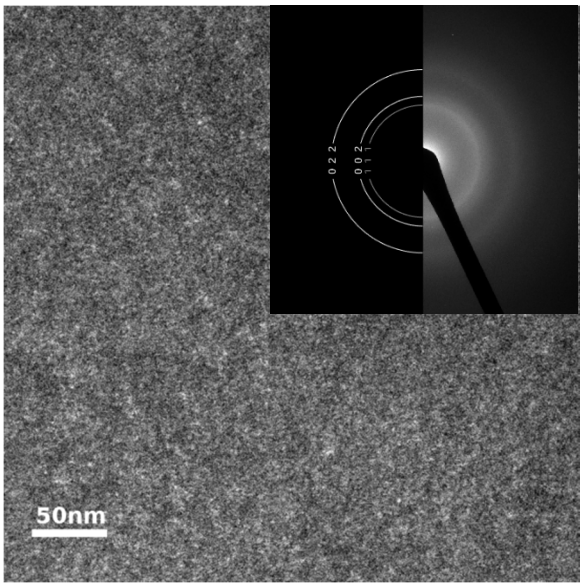

Fig. 4. Dark field microphotograph and SAED pattern (insert) of sample M100

The coating continues to grow in the same morphology if we increase the nitrogen partial pressure to 0.135Pa, as illustrated in Figure 5, although the grain size of this sample is increased to about 5nm with the higher nitrogen flow.

The orientation of the few nanometer sized grains is random, and the hardness of the sample M037 was measured to be 1863HV, a slight increase from sample M100.

The morphology of the thin film changes when we reach a critical nitrogen partial pressure, although we found that it is not detectable in terms of macroscopic measureable parameters during the sputtering process. The size of the crystallites in sample M062 (Figure 6) is reduced again, and the hexagonal AlN phase reappears and dominates the structure.

The FCC TiN phase is present, but it has a small contribution. The 0002 planes of the

hexagonal phase are oriented parallel with the substrate surface. The coating exhibits fiber-like growth morphology, in the interior of the fibers the grains are positioned in close orientation to each other.

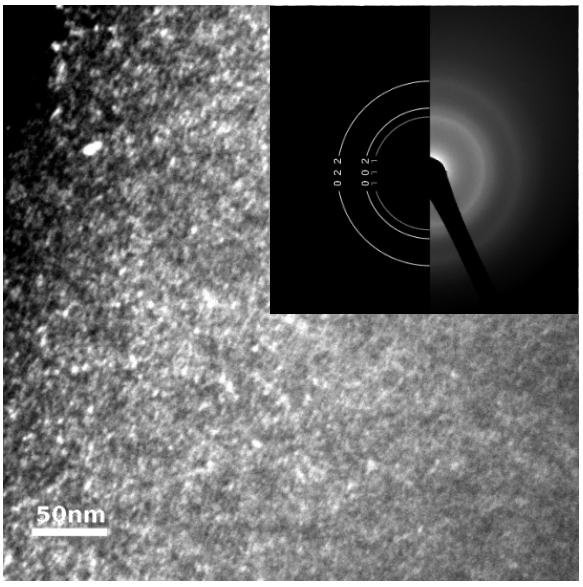

Fig. 5. Dark field microphotograph and SAED pattern (insert) of sample M037

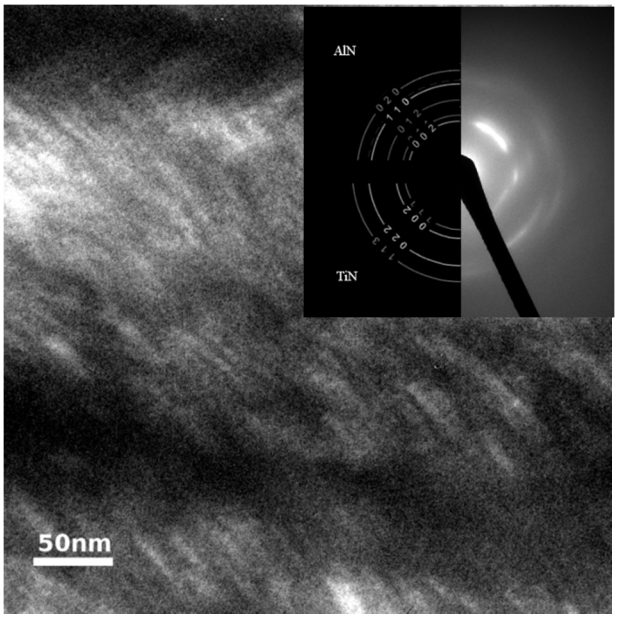

Fig. 6. Dark field microphotograph and SAED pattern (insert) of sample M062

At higher nitrogen partial pressure in sample M64 (Figure 7) both phases are present in the same textured orientation the only difference is that while the hexagonal phase is oriented with 0002 planes parallel to the substrate surface, the FCC TiN phase is oriented with 111 planes parallel to the same surface. There is a small increase in grain size, as the radial dimension of the diffraction spots is reduced.

At the highest partial pressure used in our experiments the grain size further increased (Sample M066 Figure 8). Both the hexagonal and FCC phases are present, in the same orientation as in sample M64.

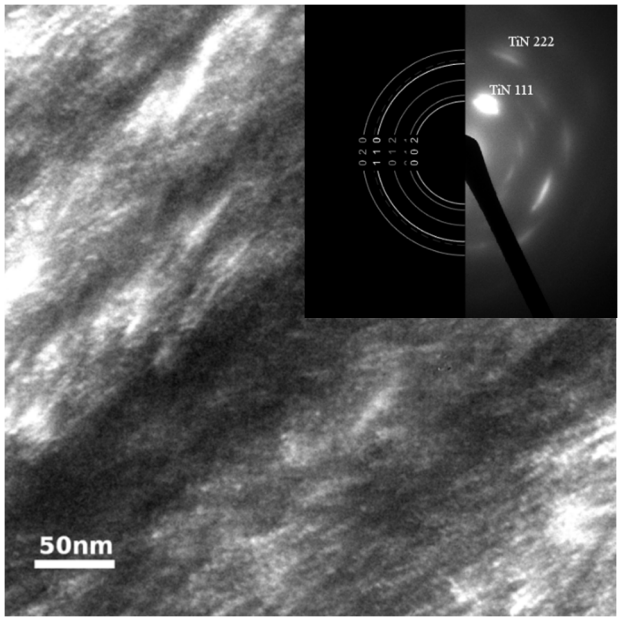

Fig. 7. Dark field microphotograph and SAED pattern (insert) of sample M064

A fine lamellar feature is also observable in the dark field micrograph on Figure 8. The microhardness of sample M066 was found to be 1640HV.

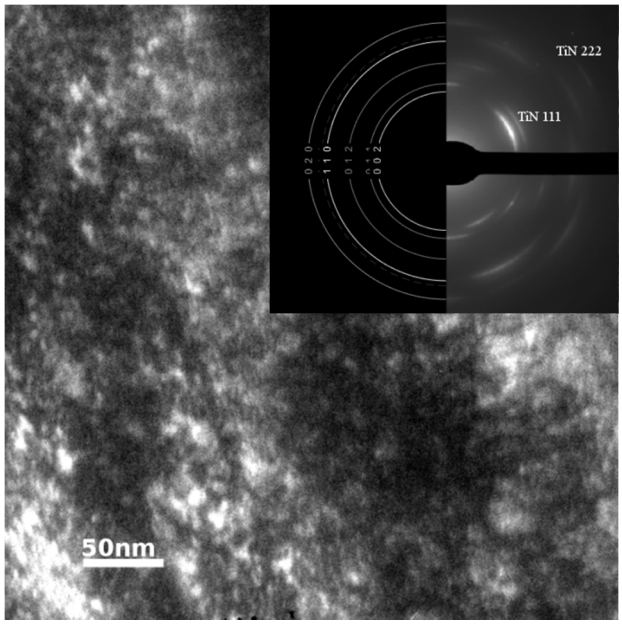

Fig. 8. Dark field microphotograph (up) and SAED pattern (insert) of sample M066

In conclusion these coatings if deposited at sufficiently low nitrogen flows will grow as nanometric size hexagonal AlN-like grains, part of which will be oriented with their 002 planes parallel to the substrate surface. Between these grains, nanometric FCC TiN grains will be present but without preferred orientation.

At higher nitrogen flow, no more hexagonal AlN grains will grow, and the whole coating will be formed by randomly oriented FCC TiN grains.

At a sufficiently high nitrogen flow, the hexagonal grains will reappear, with the same orientation as before, and some of the FCC TiN grains will remain, but they will be oriented with the 111 plane parallel to the surface.

Considering these findings about this sample set, we prepared samples with stepwise rising and decreasing nitrogen flow. The step for the nitrogen flow was chosen to be 1sccm, and the time for each sublayer was 600seconds.

The numbers presented in the scale of Figure 9 are the corresponding nitrogen flow rates for each sublayer in sccm.

Sample M085 was prepared at 400^0C, sample M86 at 500^0C.

The corresponding sublayer morphologies are in good agreement with the expected ones for them in case of sample M085, based on the previous sample set.

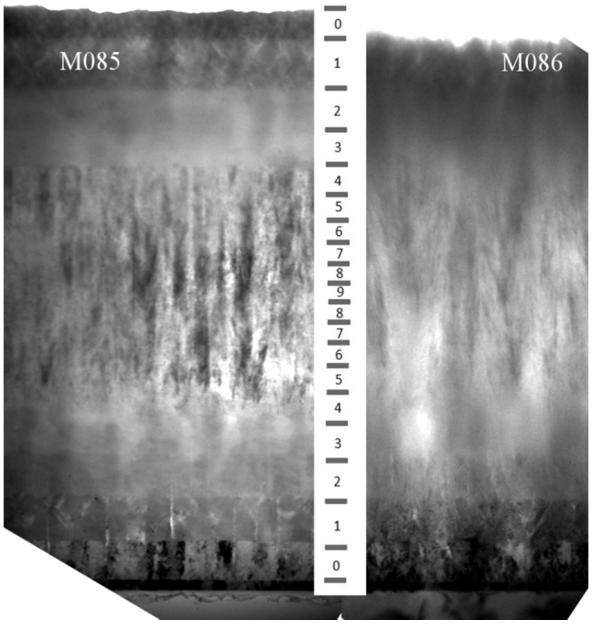

Fig. 9. Bright field microphotograph of samples M085 and M086 with illustrated nitrogen flow rates

We can conclude from the bright field microphotographs, that the nitrogen flow introduced in the system at any given time, a specific morphology will be created.

The main difference between the two latter samples in terms of morphology is the range of nitrogen partial pressure where the FCC TiN phase grains are present. At higher temperature, this phase is present on a much narrower nitrogen partial pressure range, and the limits of this range are different in function of temperature.

6. CONCLUSIONS

We prepared several samples for studying the formation morphology of TiAlSiN coatings under specific circumstances.

We observed the changes in morphology of the coatings in function of nitrogen partial pressure and temperature.

6. ACKNOWLEDGEMENTS

Some of the investigations were performed in a CM 20 Philips 200kV TEM electron microscope by Professor P.B. Barna from RITPMS, Budapest. Contribution given by Professor P.B. Barna electron microscopy and valuable discussions are highly appreciated.

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Unele observații asupra straturilor subțiri TiAlSiN ternare realizate în condiții particulare

Nevoia de acoperiri rezistente la uzură cu performanțe mai înalte a direcționat atenția de la TiN la extensia sistemului de materiale cu elemente adiționale precum Al și Si. Această lucrare prezintă concluziile noastre în legătură cu acest sistem de materiale.

Am studiat evoluția morfologiei creșterii în ceea ce privește debitul de azot și temperatură pentru a urmări schimbările care apar în structura acoperirilor. Acoperirile noastre au avut o creștere texturată slab la cele mai scăzute fluxuri de azot. Această structură s-a transformat într-una nanocristalină difuză orientată în mod aleatoriu, la creșterea debitului de azot în timpul depunerii. Morfologia acoperirii s-a schimbat din nou într-o formă texturată la debite de azot și mai mari. Am constatat că punctele de comutare pentru aceste tranziții depind de temperatură.

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