

## Microhardness of Ti-Al-Si-N Coatings Deposited by DC Reactive Magnetron Sputtering

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### Abstract

*(Ti,Al,Si)N coatings were deposited on HSS or silicon substrates by DC reactive UM magnetron sputtering. The target was Ti-Al-Si (50 at.% Al, 25 at.% Ti, 25 at.% Si). There were deposited several coatings by varying the nitrogen flow rate. The microhardness of (Ti,Al,Si)N coatings was measured using a CV-400 AAT hardness tester and was found in 4...24 GPa range. XTEM investigation showed the columnar microstructure for coatings deposited in the absence of reactive gas and the nanocrystalline microstructure for (Ti,Al,Si)N coatings.*

### 1. Introduction

Veprek, in his well known review paper “Different approaches to superhard coatings and nanocomposites” [1] showed that there are two mechanisms that leads to the increase of hardness in hard and superhard coatings.

One is hardness enhancement by energetic ion bombardment. This phenomenon is due to a complex, synergistic effect involving a decrease of crystallite size, densification of the grain boundaries, formation of Frenkel pairs and other point defects, and built-in biaxial compressive stress.

The second is the mechanism of hardness enhancement by the formation of a stable nanocomposite structure due to self-organization upon spinodal phase segregation. This concept is based on a strong, thermodynamically driven, and diffusion rate-controlled (spinodal) phase segregation that leads to the formation of a stable nanostructure by self-organization. In the case of superhard, thermally highly stable nanocomposites the dislocation activity is absent. These materials consist of a few-nanometer

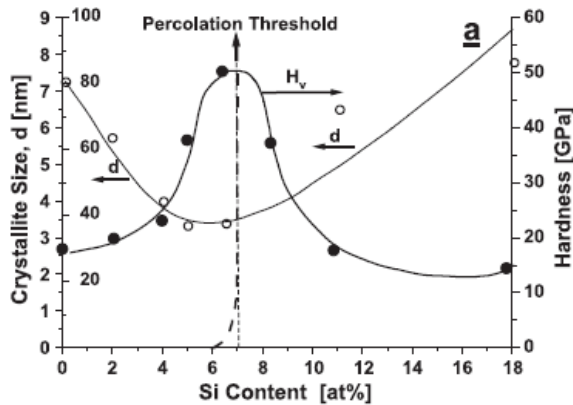
small crystallites of a hard transition metal nitride (or carbide, boride) “glued” together by about one-monolayer-thin layer of nonmetallic, covalent nitride such as Si<sub>3</sub>N<sub>4</sub>, BN (or in the case of carbides by excess carbon, CN<sub>x</sub>, and others). Depending on the crystallite size in the given material, the effects mentioned above may hinder the dislocation activity. These coatings, when correctly prepared, posses an unusual combination of mechanical properties, such as a high hardness of 40 to 100 GPa, high elastic recovery of 80% to 94%, elastic strain limit of >10%, and high tensile strength of 10 to ≥40 GPa that is approaching the ideal strength off low-free materials. Moreover, the nanostructure and the concomitant superhardness (measured at room temperature after each annealing step) remain stable up to ≥1100 °C. Highest hardness enhancement upon energetic ion bombardment is obtained in refractory hard ceramic coatings deposited at a relatively low temperature of about ≤300 °C. At a higher temperature, the hardness enhancement decreases and completely vanishes above 600–700 °C, whereas that of the superhard nanocomposites remains unchanged upon annealing up to 1100 °C.

In nc-TiN/a-Si<sub>3</sub>N<sub>4</sub> and analogous systems, such as nc-W<sub>2</sub>N/a-Si<sub>3</sub>N<sub>4</sub>, nc-VN/a-Si<sub>3</sub>N<sub>4</sub>, nc-TiN/a-BN, and others, spinodal phase segregation is thermodynamically driven by a high activity (partial pressure) of nitrogen, and rate-controlled by diffusion that requires a sufficiently high temperature. A sufficiently high activity of nitrogen (partial pressure of >10<sup>-5</sup> bar) is needed in order to provide the necessary thermodynamic driving force for spinodal decomposition to occur during deposition that results in the formation of an nc-TiN/a-Si<sub>3</sub>N<sub>4</sub> nanocomposite with a small and regular crystallite size. The hardness reaches a maximum of 50–60 GPa at a silicon content of about 8–10 at.% (Fig. 1) when the nanocrystals of the transition metal nitrides are covered with about one monolayer of silicon [1].

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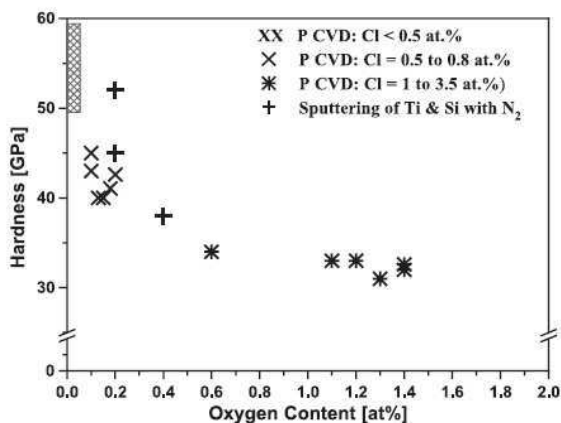
**Keywords:** plasma, chemical vapor deposition, nanocrystalline microstructure

These hardnesses are achieved when the deposition conditions are properly chosen so as to provide a high thermodynamic driving force and sufficiently high deposition temperature, and the energy of ions reaching the surface of the growing film is low.



**Fig 1. Dependence of the crystallite size and hardness on the total silicon content in nc-TiN/a-Si<sub>3</sub>N<sub>4</sub> for coatings deposited by plasma chemical vapor deposition (P CVD) upon low-energy ion bombardment [1]**

It is important to understand the detrimental role of impurities which, when incorporated into the coatings during the growth, make it impossible to achieve superhardness or even any hardness enhancement at all. The most dramatic degradation of the hardness is caused by oxygen as illustrated in Fig. 2 where the maximum achievable hardness for the optimum Si<sub>3</sub>N<sub>4</sub> content is showed vs. the oxygen impurity concentration [1].



**Fig 2. Dependence of the maximum achievable hardness on the oxygen impurity content for nc-TiN/a-Si<sub>3</sub>N<sub>4</sub> coatings [1]**

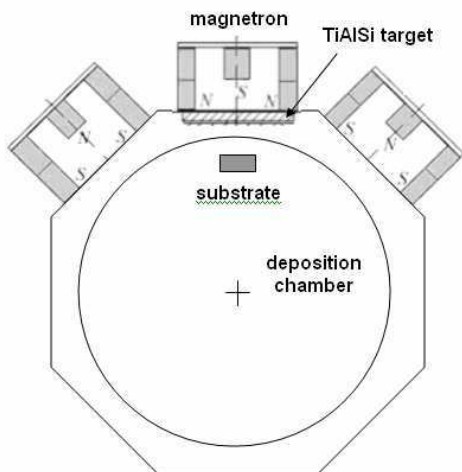
Prochazka showed that the maximum achievable hardness in nc-TiN/a-Si<sub>3</sub>N<sub>4</sub> nanocomposites deposited by reactive magnetron sputtering under a sufficiently high nitrogen pressure of  $\geq 0.001$  mbar (a higher pressure is desirable, but its use limits the deposition rate) and deposition temperature of 550–650 °C is controlled by the oxygen impurity concentration [2].

Regarding the microstructure, coatings deposited by PVD at relatively low temperatures of 300–600 °C have a columnar morphology whose development is described by the Thornton structure zone diagram. When superhard nanocomposites with the optimum composition are formed, this columnar structure vanishes. The development of an isotropic and dense nanostructure upon the formation of stable superhard nanocomposites is an important result because the columnar morphology, even if within the dense T-zone, still suffers in terms of mechanical properties due to weaker bonding between the columns. Therefore, the complete vanishing of the columnar morphology in the nanocomposites deposited by PVD is important to the excellent mechanical properties of these nanocomposites. Veprek, citing the work of Karvankova et al. [2], showed that although the morphology of the nanocomposites with the highest hardness deposited by magnetron sputtering appears isotropic, a more detailed investigation by TEM reveals that there is still a sign of a slightly columnar, quite dense morphology [1].

The research presented in the present paper represents our first experimental steps in order to develop hard Ti-Al-Si-N coatings by reactive unbalanced magnetron sputtering.

## 2. Experimental

The experimental research was performed using a custom made DC reactive unbalanced magnetron sputtering system for co-deposition process of multiphase and multielemental compound. Although the system has the possibility to use three magnetron sources, for these experiments only one target was used: Ti-Al-Si (50 at.% Al, 25 at.% Ti, 25 at.% Si). Figure 3 presents the experimental setup. There were deposited several 5-6  $\mu\text{m}$  thick (Ti,Al,Si)N coatings on HSS substrates using a sputtering power of magnetron of 500 W and the same bias voltage ( $U_s = -75$  V) and substrate temperature ( $t_s = 400$  °C) for all samples. The flow for argon gas was 6 sccm. The flow for the nitrogen gas was 0...6 sccm. Total deposition time was approx. 90 min. Prior to deposition a base pressure of  $5.0 \cdot 10^{-4}$  Pa was established. Table 1 presents the main deposition parameters for these samples.

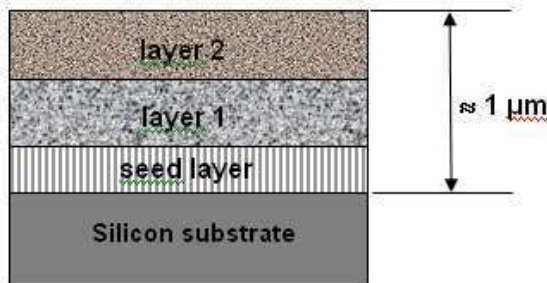


**Fig 3. Schematic illustration of the experimental setup**

**Table 1. Deposition parameters for thick coatings**

Sample	Magnetron power $P_{\text{Ti-Al-Si}}$ [W]	Gas flow $q_{\text{N}_2}$ [sccm]	Substrate temperature $T_s$ [°C]	Bias voltage $U_s$ [V]
TiS-01	500	-	400	-75
TiS-04	500	2	400	-75
TiS-06	500	3	400	-75
TiS-03	500	4	400	-75
TiS-05	500	5	400	-75
TiS-02	500	4	400	-75

Also, there were deposited two thin coatings (1  $\mu\text{m}$  thick) on silicon substrates, in order to be investigated by TEM on the samples prepared using the technique of ion beam thinning. The sample TiS-01/b was deposited in the same condition like TiS-01. The sample TiS-08 is a tri-layer one (fig. 4).



**Fig 4. Schematic illustration of the thin tri-layer Ti-Al-Si-N coating (sample TiS-08)**

On the silicon substrate a TiAlSi seed layer of 200 nm was grown, and then the nitrogen gas was introduced in the deposition chamber at a flow rate of 1 sccm leading to the formation of a Ti-Al-Si-N layer. At the surface of the sample another Ti-Al-Si-N layer was deposited with a flow rate of nitrogen of 1,5 sccm. Table 2 presents the deposition parameters for these thin coatings.

**Table 2. Deposition parameters for thin coatings**

Sample	Mag netron power $P_{\text{Ti-Al-Si}}$ [W]	Gas flow $q_{\text{N}_2}$ [sccm]	Substrate temp. $T_s$ [°C]	Bias voltage $U_s$ [V]
TiS-01/b	500	-	400	-75
TiS-08 tri-layer	500	seed layer: - layer 2: 1 layer 3: 1,5	400	-75

Vickers micro hardness was measured using a CV-400 AAT micro hardness tester, with a load of 25 gf and 10 s for holding time for thick coatings and a load of 10 gf and 10 s for holding time for thin coatings.

It has been noticed by several researchers in the past that, in order to measure the hardness of hard coatings on softer substrate correctly, the maximum indentation depth must not exceed 10% of the thickness of the coating because above this value, plastic deformation occurs in the softer substrate such as steel. Therefore, in order to avoid possible artifacts that may falsify the correct value of hardness, one has to use a relatively high load of 30–150 mN (3...15 gf), with an indentation depth of  $\geq 0,3 \mu\text{m}$  that, however, must not exceed about 5% of the thickness of the coatings. To meet these requirements,  $\geq 6 \mu\text{m}$  thick coatings are needed [2].

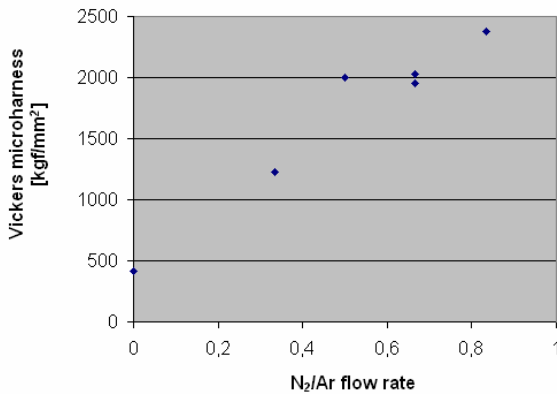
### 3. Results and conclusions

Table 3 presents the results of Vickers microhardness test applied on coatings. In figure 5 the values of microhardness are plotted vs.  $\text{N}_2/\text{Ar}$  gases flow rates. It is to discuss here that the values of Vickers microhardness for thick coatings (5...6  $\mu\text{m}$  thickness) are obtained in correct conditions having in mind the necessary load force and maximum indentation depth. In case of thin coatings (1  $\mu\text{m}$  thickness) the values of of Vickers microhardness have to be take with some care, because of the fact that

maximum indentation depth exceeded 10% off thickness of the coatings. In this case the measured values for TiS-01/b and TiS-08, (presented in Table 3 but not plotted in Fig. 5) are influenced by the silicon substrate hardness. It is expected that true hardness of the coatings to have higher values than ones that are measured.

**Table 3. Results of Vickers microhardness test**

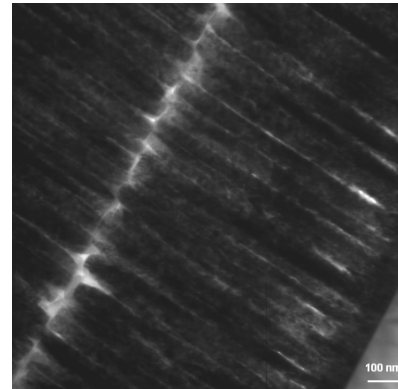
Sample	Nitrogen gas flow $q_{N_2}$ [sccm]	Vickers microhardness HV [kgf/mm <sup>2</sup> ]
TiS-01	-	413
TiS-04	2	1230
TiS-06	3	1998
TiS-03	4	1957
TiS-05	5	2378
TiS- 02	4	2027
TiS-01/b	-	375
TiS-08	-; 1; 1,5	1551



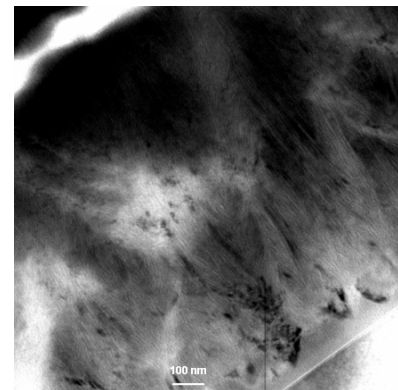
**Fig 5. Vickers microhardness as a function of N<sub>2</sub>/Ar gases flow rates**

The cross sectional microstructure of TiS-01/b coating is showed in Fig. 6. The coating is developed in the absence of reactive gas, so is a Ti-Al-Si metallic one. It consists on columnar crystalline grains. Because of the weak bonding between columns the mechanical properties of such coatings are poor, including hardness, as results also from our test (Table 3).

The cross sectional microstructure of TiS-08, presented in Fig.7, seems to be a nanocrystalline one. In the presence of nitrogen, the columnar microstructure vanishes, but there is still an appearance of a slightly columnar, dense morphology.



**Fig. 6. BF XTEM of TiAlSi coating showing its columnar microstructure (sample TiS-01/b)**



**Fig. 7. BF XTEM of (Ti,Al,Si)N coating showing its nanocrystalline microstructure (TiS-08)**

In conclusion the measured hardness for our coatings was found in the 4...24 GPa range. For superhard nanocomposite materials the hardness is  $\geq 40$  GPa. In order to develop nc-(Ti,Al)N/a-Si<sub>3</sub>N<sub>4</sub> we have to fine tune the sputtering system, to be able to maintain proper process parameter during deposition and to control much better the amount of impurities, especially oxygen, because if the oxygen impurity content in the coatings is larger than about 0.2–0.3 at.%, the hardness of  $\geq 40$  GPa cannot be reached.

### 3. References

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