Diamond coatings on SiAlON ceramic cutting tool with high adhesion

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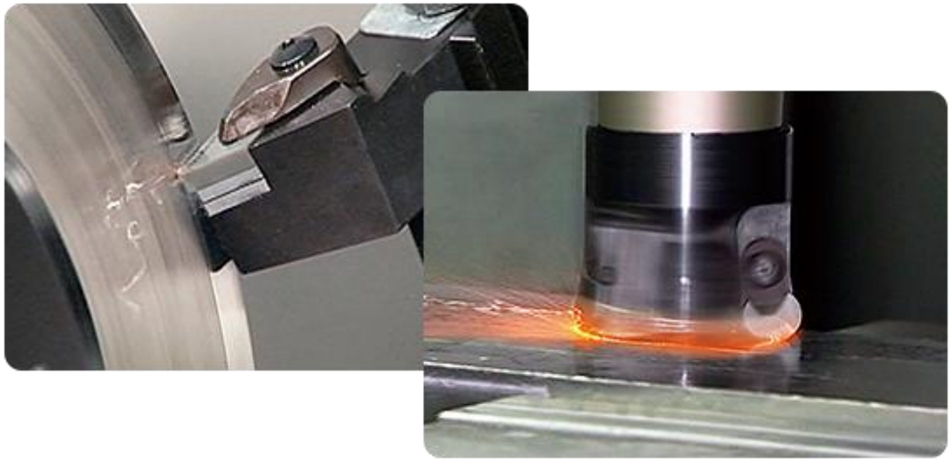
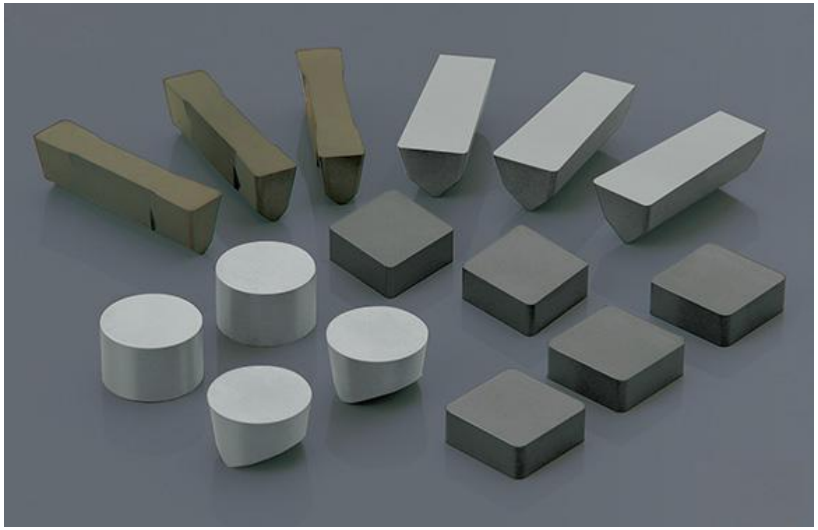
Outline

- Coating of cutting tools with diamond
- SiC+double layer approach to diamond deposition
- Diamond synthesis and characterization
- Tribology, dry cutting and scratching tests
- Conclusions

SiAlON cutting tools





Cutting inserts of SiAlON ceramics ("*NTK Cutting Tools*", USA)

- It exhibits high abrasion and chemical wear resistances,
- It is widely used cutting tools material, especially in turning of gray cast irons and superalloys

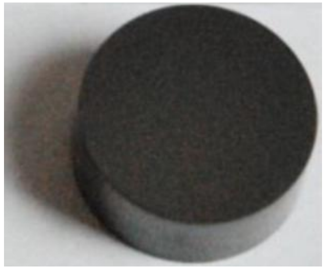
Wear resistance of diamond is up to 6 times higher than that of SiAlON and up to 5 times higher than of WC-Co hard alloy tools

Samples of SiAlON ceramics ("LSPS MSTU STANKIN", Moscow)

Samples of SiAlON ceramics

- N1-1: α-SiAlON 90% + β-SiAlON 10%, T(sintering)=1500°C (LSPS MSTU STANKIN),
- N1-2: α-SiAlON 90% + TiN 10%, T(sintering)=1800°C (LSPS MSTU STANKIN),

Diameter of 20 mm, height of 3 mm



Diameter of 20 mm, height of 8 mm

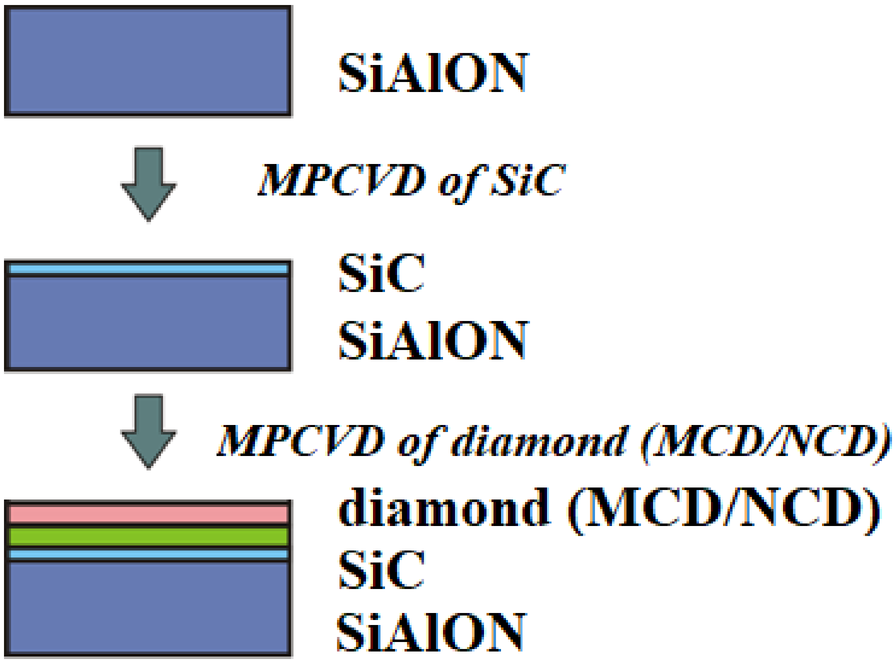
- N2: TaeguTec (South Korea),

10×10×8 mm

- N3: alloy CC6060 of Sandvik Coromant (Sweden)

WC-Co plates and chemical vapor deposition of diamond (CVD)

Scheme of synthesis



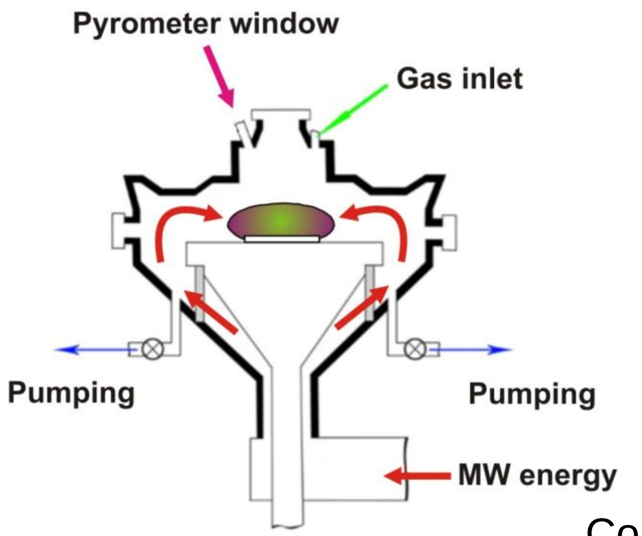
Diamond coatings on cutting tools are usually <u>single layer.</u> We propose multilayer coatings.

Diamond coating are usually deposited on WC-Co tools. We propose deposition on SiAlON tools.

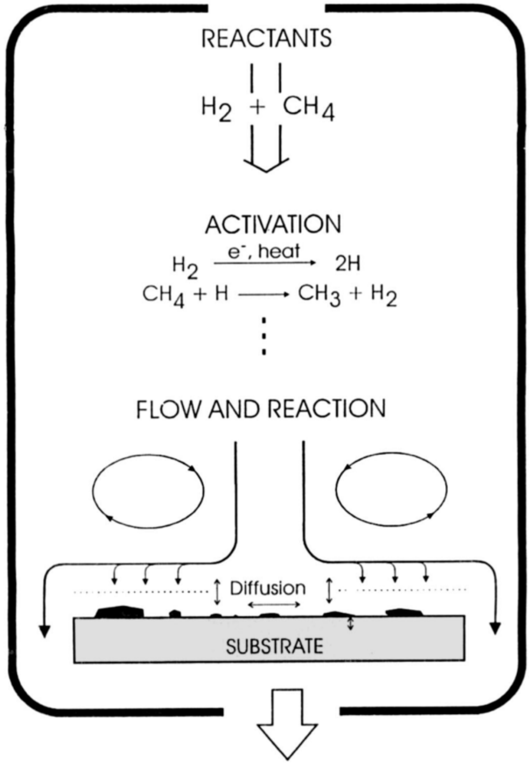
We propose the most commonly used technique – MPCVD to cover cutting tools with diamond films using plateholder approach which support diamond adhesion and decrease the edge effect of CVD plasma.

≈95% of CVD reactors are MPCVD – ≈98% of WC-Co inserts coated with diamond in HFCVD reactors because of poor adhesion after MPCVD

Chemical vapor deposition of diamond out of gaseous phase

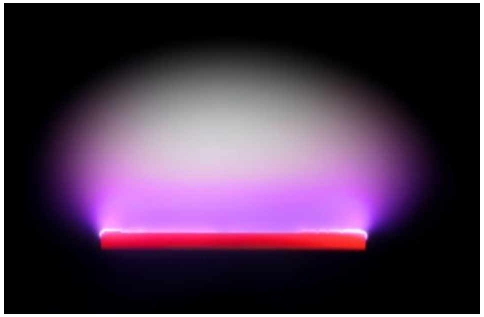


- radicals CH_3 and C_2 are the most important in the reaction chain at the surface
- atomic hydrogen H – selective etching of graphite phase (sp^2 carbon)



Growth conditions

Common gas mixture: 1-4% CH_4 + H_2
Pressure: 50-120 Torr
Power: microwave: 2-6 kW
Substrate temperature ≈ 700-900ºC
Growth rate ≈ 1-3 μm/hour
Gas flow rate: 500 cm^3/min



Methods of the gas activation during CVD:

- **Microwave plasma**

others: hot filament, DC plasma jet, laser plasma, etc.

Diamond seeding of a substrate surface

The problem of a diamond nucleation

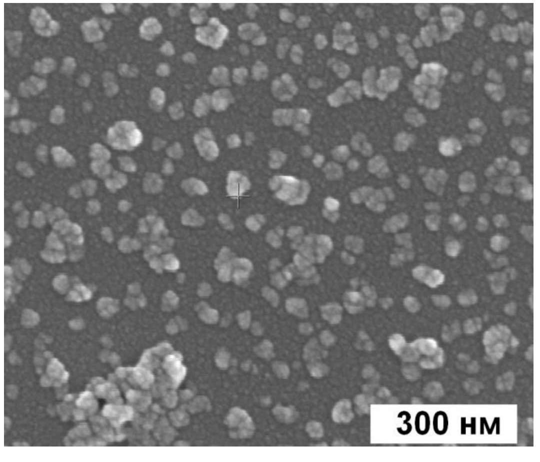
● High surface energy of diamond + thermodynamic instability under the CVD conditions (~800ºC, ~0.1 atm): diamond is stable at ~2000ºC, >50000 atm
→ self-nucleation is hindered both at flat and at developed surfaces;

● One need to input the diamond nucleation centers – seeding with nucleation density of up to 10^{11} grains/cm^2;

● Seeding is key issue to produce a continuous film on complex 3-d surfaces of cutting tools

Centrifuge
“SPIN150i NPP”

Nanodiamond suspensions with water, isopropanol, acetone

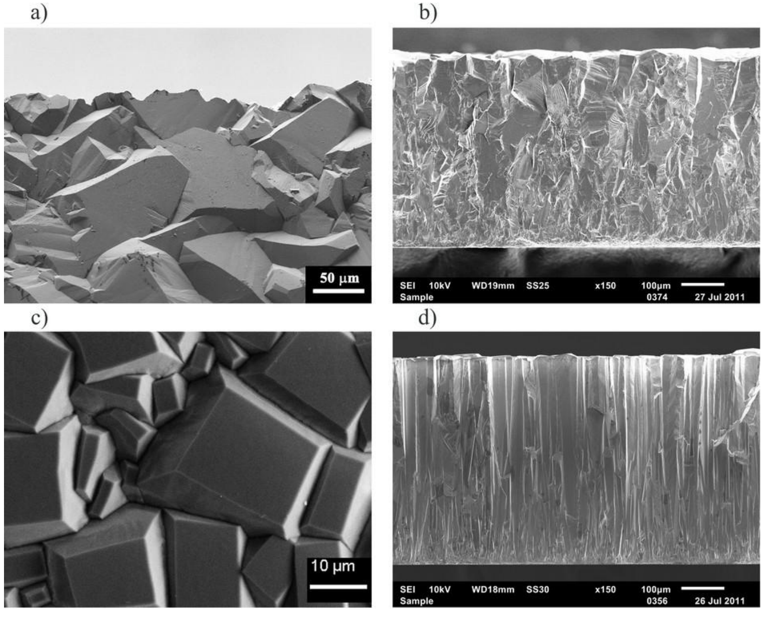


Seeded Si substrate

**“white”
(no sp^2 carbon)**

Continuous polycrystalline films

**“black”
(up to 0.1% sp^2 carbon)**



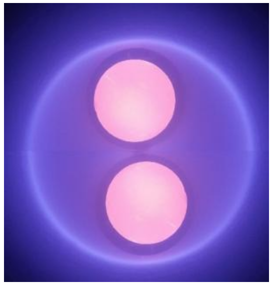
Scheme for covering of the SiAlON samples with diamond

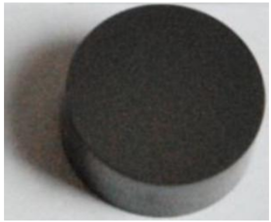
1st step of producing of the diamond coated SiAlON samples is MPCVD growth of SiC (interlayer for increasing of the adhesion): $H_2/CH_4/SiH_4$ gas mixture, SiH_4/CH_4 = 20%, the SiAlON substrate temperature was 1000°C, the growth duration was 4 hours,

2nd step is the SiAlON seeding in centrifuge to distribute diamond nucleation centers: the nanodiamond suspension (5 nm in size, “Daicel”) spreading under 3000 rpm rotation

3rd step is the diamond film deposition under the SiAlON temperature was 900°C, the gas pressure was 55 Torr
2.5 hours of MCD growth regime – 96% H_2+4% CH_4 {*ADHESION*}
2.5 hours of NCD growth regime – 92% H_2+4% CH_4+4% N_2 {*ROUGHNESS*}

Microwave plasma CVD system “*ARDIS-100*” (2.45 GHz), Optosystems Ltd., Troitsk, Russia





The SiAlON substrates (*LSPS MSTU STANKIN*) in process of diamond deposition: a view through the top quartz window of the microwave reactor (a) and through the side window (b); the SiAlON substrate with a deposited diamond film (c)

Patent of Russian Federation

"Microwave plasma reactor for uniform nanocrystalline diamond film deposition"

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Название
[EN] MICROWAVE PLASMA REACTOR FOR OBTAINING A HOMOGENEOUS NANOCRYSTALLINE DIAMOND FILM
[RU] СВЧ плазменный реактор для получения однородной нанокристаллической алмазной пленки

#10 in Rospatent rating of the best 100 patents of Russia in 2018
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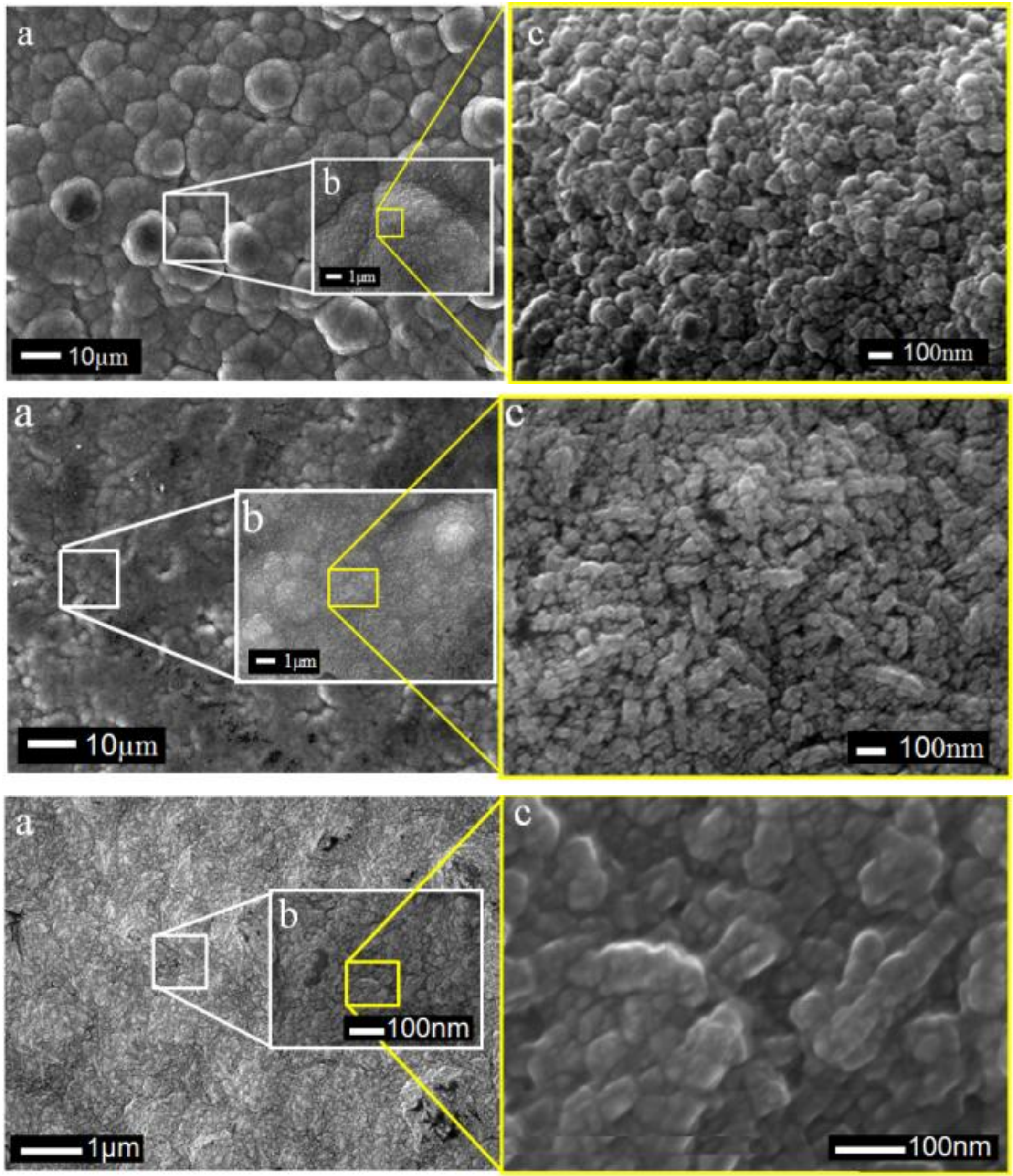
Diamond films analysis: SEM



SEM "JSM-7001F" (JEOL)

N1-1: α-SiAlON + β-SiAlON 10% (LSPS MSTU STANKIN)

Spheroidal shape clusters ,10 μm in size consisting of intergrown 10 nm grains

N1-2: α-SiAlON + TiN (LSPS MSTU STANKIN)

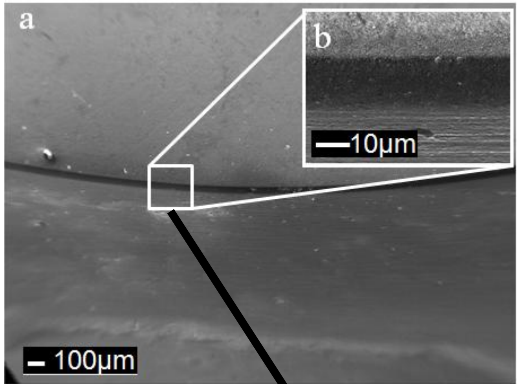
Elongated shape clusters (1:3),1 μm in size consisting of intergrown 10 nm grains

N2: SiAlON ("TaeguTec")

Elongated shape (1:3) clysters with a size of 1 μm consisting of intergrown nano-fragments of 10 nm

MCD film of comparable (10 μm) thickness should consist of 2-3 μm grains

Diamond films analysis: Raman spectroscopy

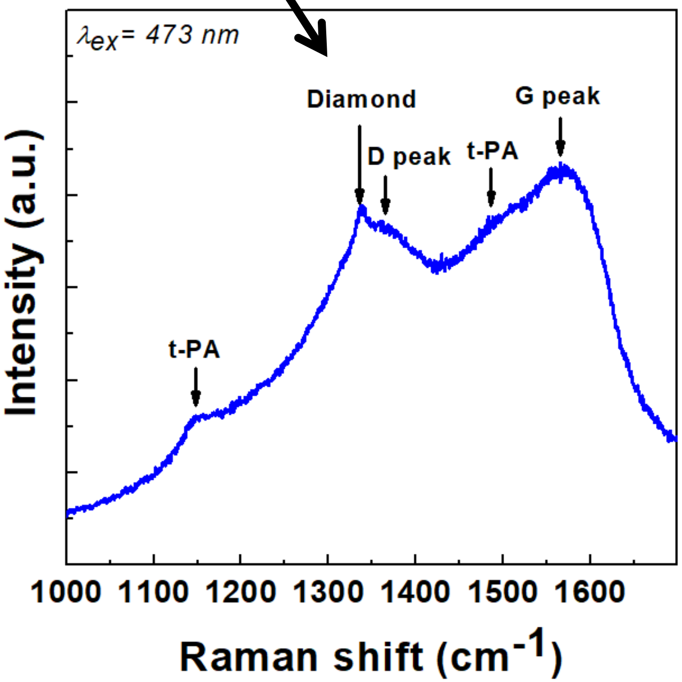


MCD/NCD diamond film on the N2 substrate edge:

(a) panoramic view, ×30,

(b) typical edge region, ×500

SEM "JSM-7001F" (JEOL)



Raman spectrum of the MCD/NCD diamond film near the cutting edge of the SiAlON substrate

"LabRAM HR800" (HORIBA-Jobin Yvon)

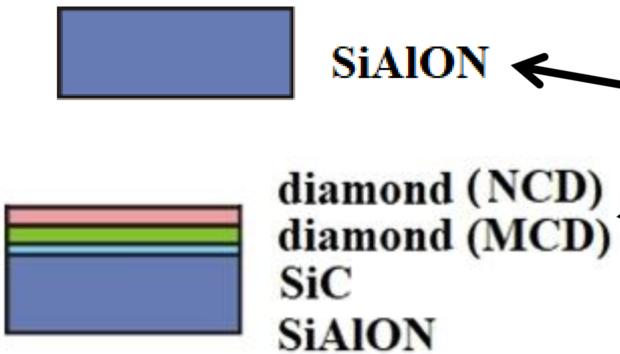
1333 cm^{-1} is the 1st order diamond Raman line with the full width at half maximum (FWHM) of 8 cm^{-1}. Other intensive lines are strong wide bands at 1350 cm^{-1} and 1590 cm^{-1} (D-peak and G-peak of amorphous sp^2 carbon) and two weak bands of trans-polyacetylene (t-PA) at 1140 cm^{-1} and 1480 cm^{-1}.

=>> Continuous nanocrystalline diamond films

Diamond films analysis: optical interferometry

"NewView 5000" (ZYGO)

Roughness R_a, R_{ms} before and after the CVD diamond growth



Sample	R_a, nm	R_{ms}, nm
N1-1	1767	2506
N1-1 diam	1599	1943
N1-2	247	114
N1-2 diam	323	434
N2	67	84
N2 diam	64	86
N3	168	219
N3 diam	151	209

SiAlON was not polished

SiAlON was polished

The value of the measured roughness values was corrected by subtracting the 2nd degree polynomial in all cases.

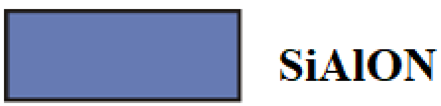
Deposition of the diamond coating significantly changes the unpolished SiAlON surface roughness. For example, for initial surface of the sample N1-1 value R_{ms} decreases by 22% after the diamond deposition (N1-1 diam), and that value of N1-2 reaches 74% decrease (N1-2 diam). And at the same time R_{ms} decrease of N2 and N3 samples is less significant and does not exceed 2.5-5%.

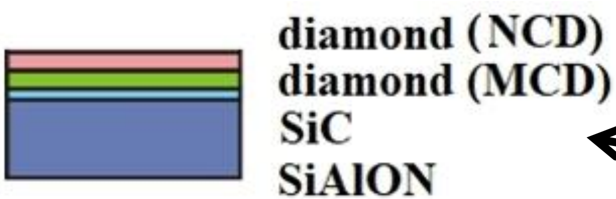
The upper nanocrystalline diamond layer decreases the initial SiAlON roughness

Diamond films analysis: tribology

"TRIBOMETER" (CSM Instruments)

Tribo-testing method: "rod-disk" scheme; track length – 4 mm; applied load – 1 N; rotation speed – 5 cm/s; Si_3N_4 counterbody ball with a diameter of 3 mm; mileage - 5000 cycles.





Sample	Wear of the counter body, $\times 10^{-6}$ $mm^3/N/m$	Friction coefficient (mean)
N1-1, N1-2	24.44	0.35
N1-1 diam	3.75	0.04
N1-2 diam	7.06	0.06
N2	15.43	0.42
N2 diam	8.29	0.09

SiAlON was not polished

SiAlON was polished

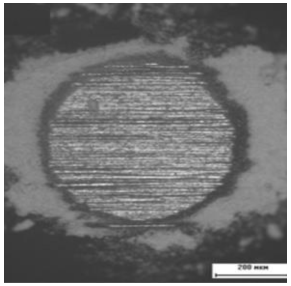
Friction coefficient μ of the SiAlON N1 and N2 are close to each other (0.35 and 0.42) despite the that their roughness differs by 25 times: R_a(N1) = 1597 nm, and R_a(N2) = 64 nm. The wear of the counter body drops by 6.5 times (N1-1 diam) or 3.5 times (N1-2 diam) downto $3.75 \cdot 10^{-6}$ $mm^3/N/m$ or $7.06 \cdot 10^{-6}$ $mm^3/N/m$ respectively owing to decrease of the friction coefficient with the NCD surface. The wear drops by 86% after the diamond deposition on N2 sample.

The SiAlON wear decreases by 3-6 times for the diamond coated samples

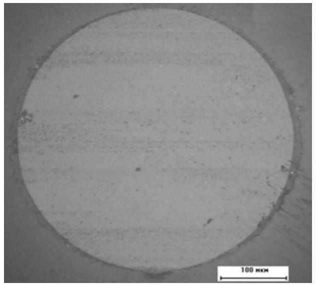
Diamond films analysis: tribology

“TRIBOMETER” (CSM Instruments)

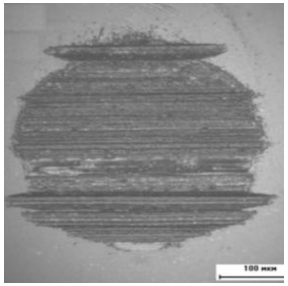
The Si_3N_4 counter body wear after the dynamic friction with:



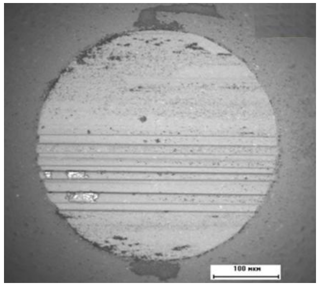
N1-1



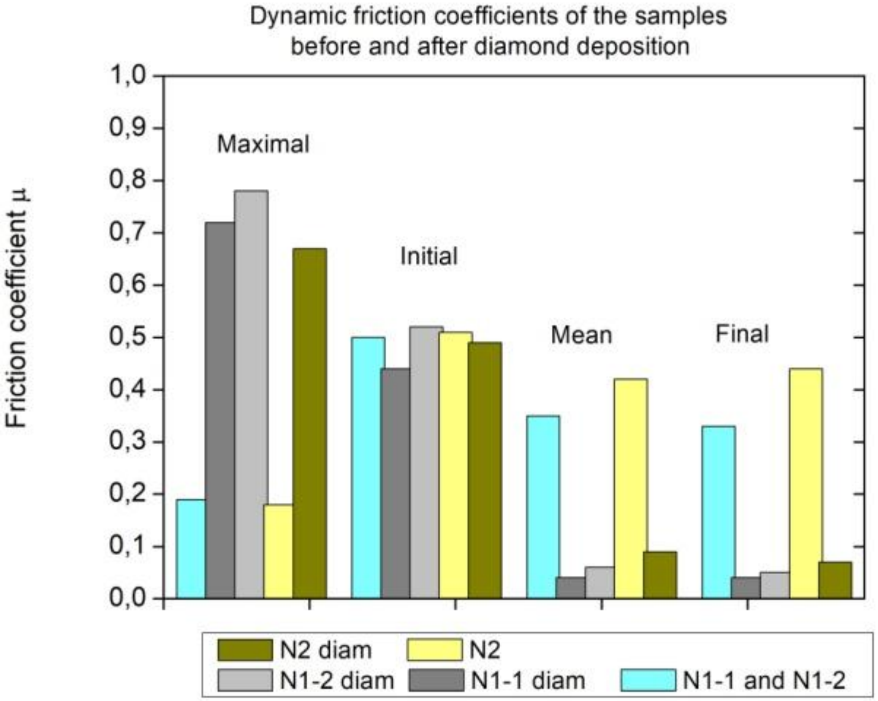
N1-1 diam



N2



N2 diam



The almost doubled wear and increased by 1.5 times μ of the sample N1-1 diam compared to the sample N1-2 diam is explained by the fact that the R_a (N1-1 diam) = 1599 nm is five times greater than R_a (N1-2 diam).

μ of the diamond coated samples have decreased by 8.8/5.8/4.7 times, and

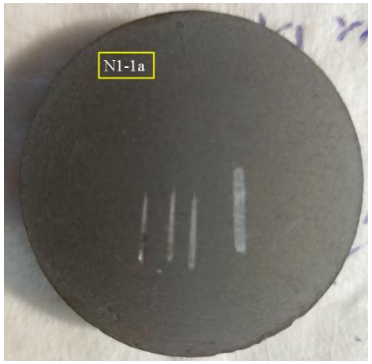
R_a of the diamond coated samples have decreased by 1.1/-0.8/1.05 times (N1-1, N1-2, N2).

The less SiAlON friction coefficient, the less wear,
but both friction and wear don’t correlate with the sample roughness

Diamond films analysis: abrasion resistance

"TRIBOMETER" (CSM Instruments)

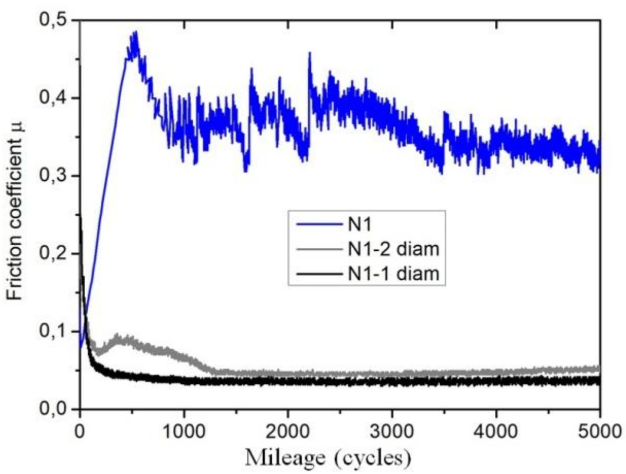
SiAlON samples with wear grooves after measuring scratching by diamond indenter :

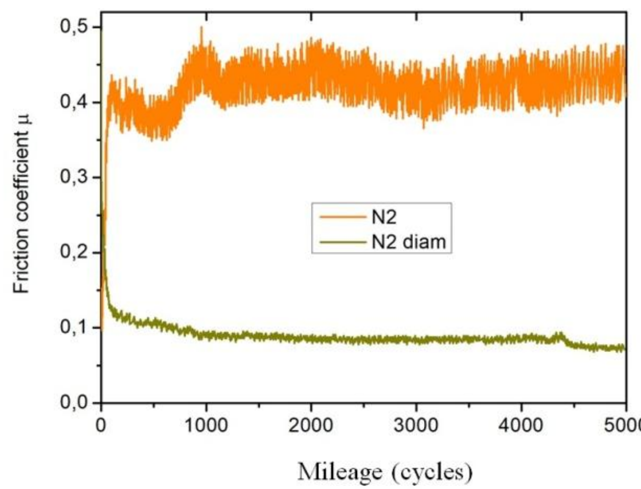


N1-1 diam

N1-2 diam

N2 diam





Experimental curves of the dynamic coefficient of friction for samples N1 and N2

Friction curves have 3 typical ranges. Namely, for N1-2 diam there are dramatic μ decrease from 0.25 to 0.07, then μ grew to 0.09 and decreased to 0.044, being stabilized at that level. That initial peak can be explained by the locking effect at the boundary between Si_3N_4 ball and sharp NCD asperities vertices in the beginning of test.

Absence of oxides on the NCD surface => water decomposition and easy sliding

Diamond films analysis: analysis of acoustic emission

"REVETEST" (CSM Instruments)

Cohesion and adhesion of the diamond coated SiAlON samples

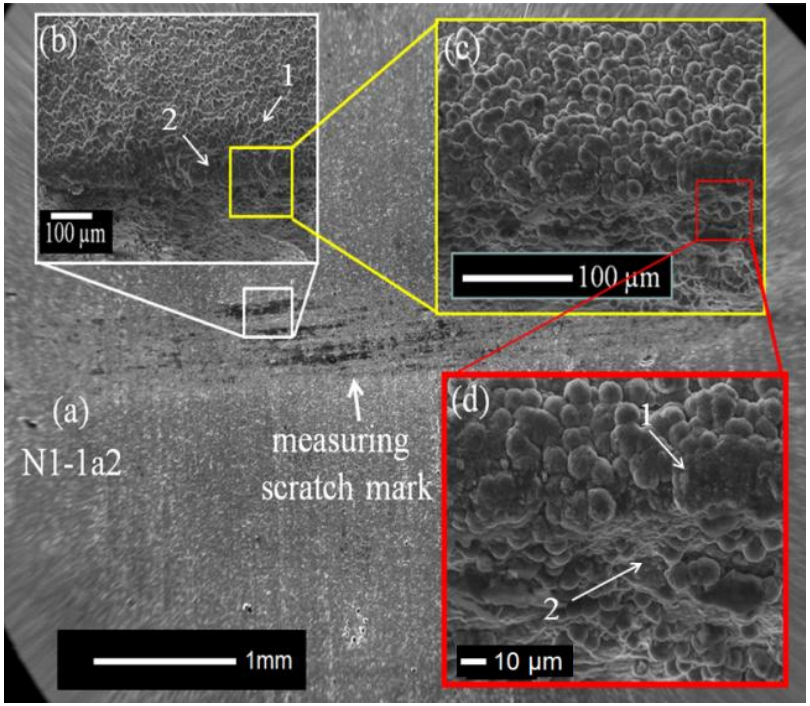
Sample	Critical load, N		Stages of destruction
	Cohe-sion	***Adhe-sion***	
N1-1 diam #1	3,8	34,7	Formation of diamond/SiAlON powder when the indenter grinds the coating protrusions. Break of the coating under the indenter at 34.7 N for N1-1 diam #1 only
N1-1 diam #2	1,0	>41	
N1-1 diam #3	1,0	>41	
N1-2 diam #1	16,0	30,1	Formation of the powder when the indenter grinds the coating protrusions for N1-2 diam #1 and N1-2 diam #2. Break of the coating under the indenter at 30.1 N and 37.0 N accordingly
N1-2 diam #2	24,1	37,0	
N1-2 diam #3	28,4	>41	
N2 diam #1	1	35,5	Formation of the powder when the indenter grinds the coating protrusions. Break of the coating under the indenter at 35.5 N for N2 diam #1 only
N2 diam #2	1	>41	
N2 diam #3	1	>41	

The best adhesion were measured for N1-1 diam and N2 diam samples: 2 of 3 scratches demonstrated adhesion value of >41 N

Diamond films analysis: analysis of acoustic emission

"REVETEST" (CSM Instruments)

SEM micrographs of the scratch #2 on the N1-1 diam sample (adhesion >41 N) after the dynamic friction with Si_3N_4 counter body

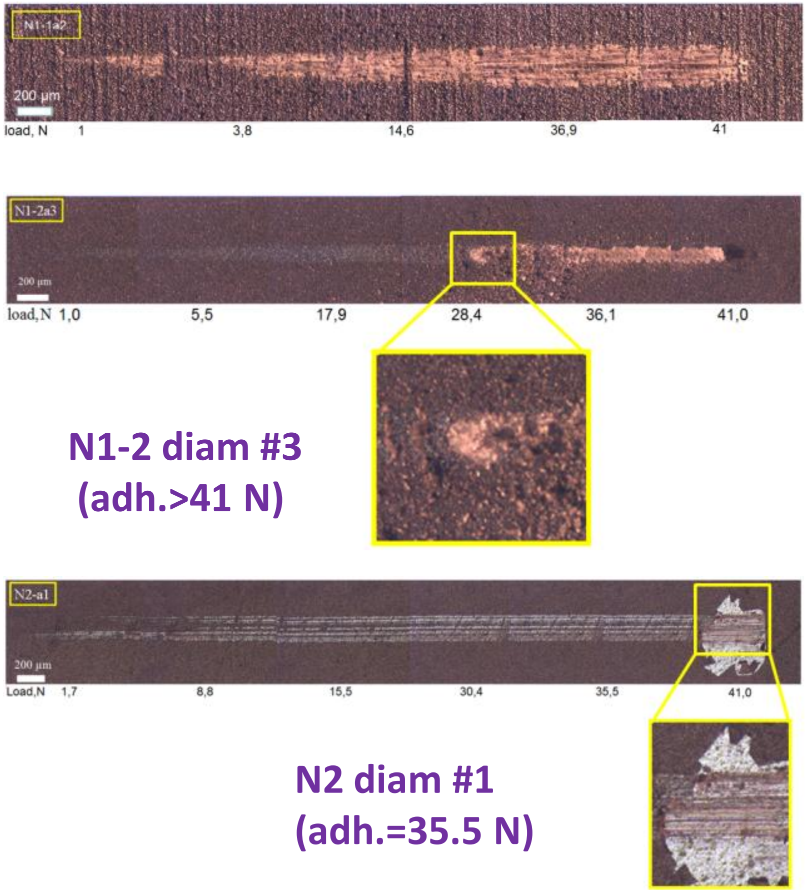


Scratch marks after the scratch testing of the CVD diamond coating on SiAlON. White scale bar at the bottom left is 200 µm

N1-1 diam #2 (adh.>41 N)

N1-2 diam #3 (adh.>41 N)

N2 diam #1 (adh.=35.5 N)

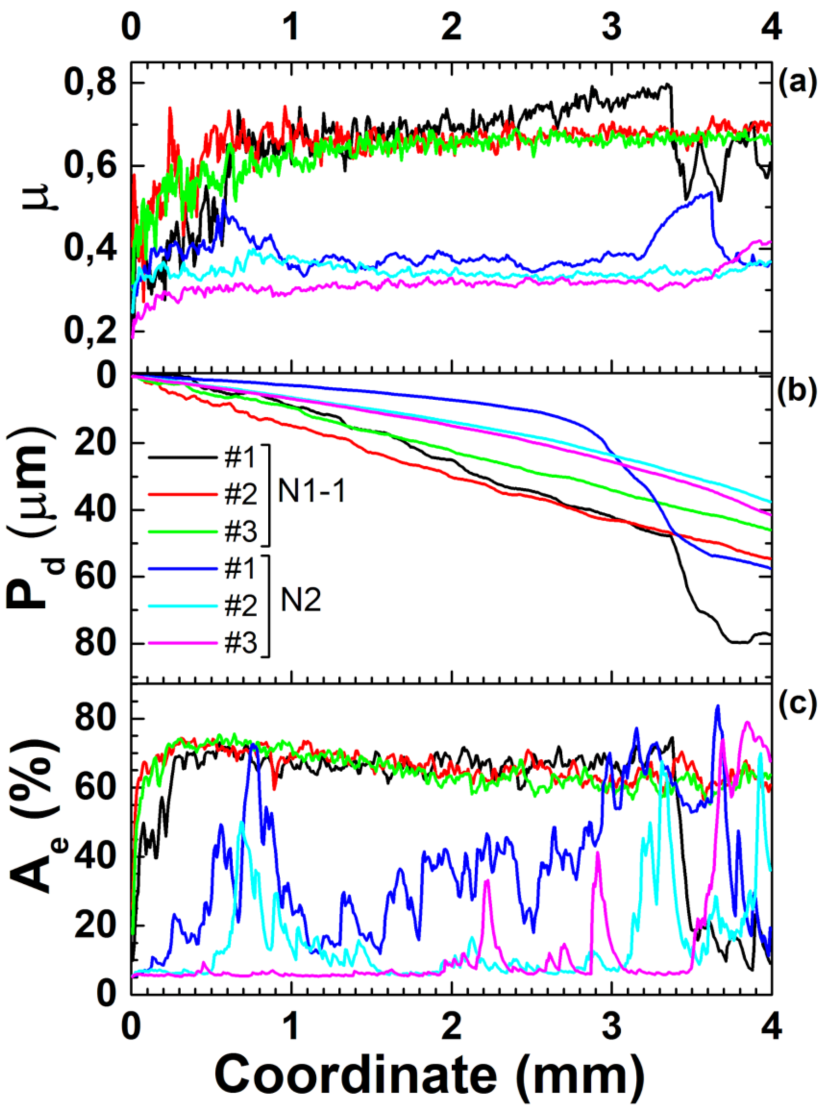


Formation of diamond/SiAlON powder when the indenter grinds the coating protrusions is the main mechanism of destruction.

Diamond films analysis: analysis of acoustic emission

"REVETEST" (CSM Instruments)

Scratch testing of CVD diamond films on biphasic SiAlON substrate where #1, #2, #3 are the scratch numbers



Coefficient of friction μ

The diamond indenter penetration depth P_d

Acoustic emission A_e

Adhesion is reduced in scratches N1-1 diam #1, N1-2 diam #1, N1-2 diam #2, N2 diam #1 downto 34.7, 30.1, 37.0, 35.5 N respectively.

For comparison, the observed adhesion of >41 N is even stronger than the adhesion of ac. 40 N for NCD coatings on Si_3N_4 ceramics deposited by HFCVD technique.

The tests have revealed neither any complete destruction of the coatings nor defects like cracks, chips or delaminations.

The observed adhesion decrease is associated both with grinding of the coating protrusions and failure of the coating under the indenter because of local slack in the substrate material.

Conclusions

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- **A three-layer SiC/MCD/NCD coating with adhesion of more than 41 N have been deposited on three types of SiAlON (α/β-SiAlON) silicon-nitride ceramic substrates from different producers (LSPS MSTU STANKIN – N1-1, N1-2; TaeguTec – N2 and Sandvik Coromant – N3) using microwave plasma chemical vapor deposition from the gas mixtures of $(H_2/CH_4/SiH_4)/(H_2/CH_4)/(H_2/CH_4/N_2)$ respectively.**

- **It has been proved that NCD layer reduces significantly roughness R_a/R_{ms} of the tool surface by 4.5% (unpolished N1-1), 10.1% (unpolished N1-2); 9.5% (polished N2) and 23.5 % (polished N3) despite a wide range of the initial SiAlON roughness R_a=2506-86 nm.**

- **The measurement of the friction coefficients μ of high-strength ceramics on Si_3N_4 counterbody before and after the diamond deposition, has revealed decrease in μ by 8.3-6.3 times: from μ=0.33-0.44 to μ=0.04-0.07, depending on the initial substrate roughness.**

- **The measurement of the counter body wear coefficient α has demonstrated a decrease of 6.5-1.9 times after the diamond deposition, namely from α(N1-1, N1-2) = $24.44 \cdot 10^{-6}$ $mm^3/N/m$ to α(N1-1 diam) = $3.75 \cdot 10^{-6}$ $mm^3/N/m$ and α(N1-2 diam) = $7.06 \cdot 10^{-6}$ $mm^3/N/m$, and from α(N2) = $15.43 \cdot 10^{-6}$ $mm^3/N/m$ to α(N2 diam) = $8.29 \cdot 10^{-6}$ $mm^3/N/m$. The less SiAlON friction coefficient, the less wear, but both friction and wear don’t correlate with the sample roughness.**

- **The scratch testing has revealed sporadic decrease in adhesion (≤ 26%) associated with grinding of protrusions and break of the coating under the indenter because of local slack in the SiAlON substrate.**

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Thank you for attention!