Oberflächenschutz und –funktionalisierung von Komposit-Werkstoffen und 3D-gedruckten Kunststoffen durch bei Raumtemperatur abgeschiedene Plasmabeschichtungen

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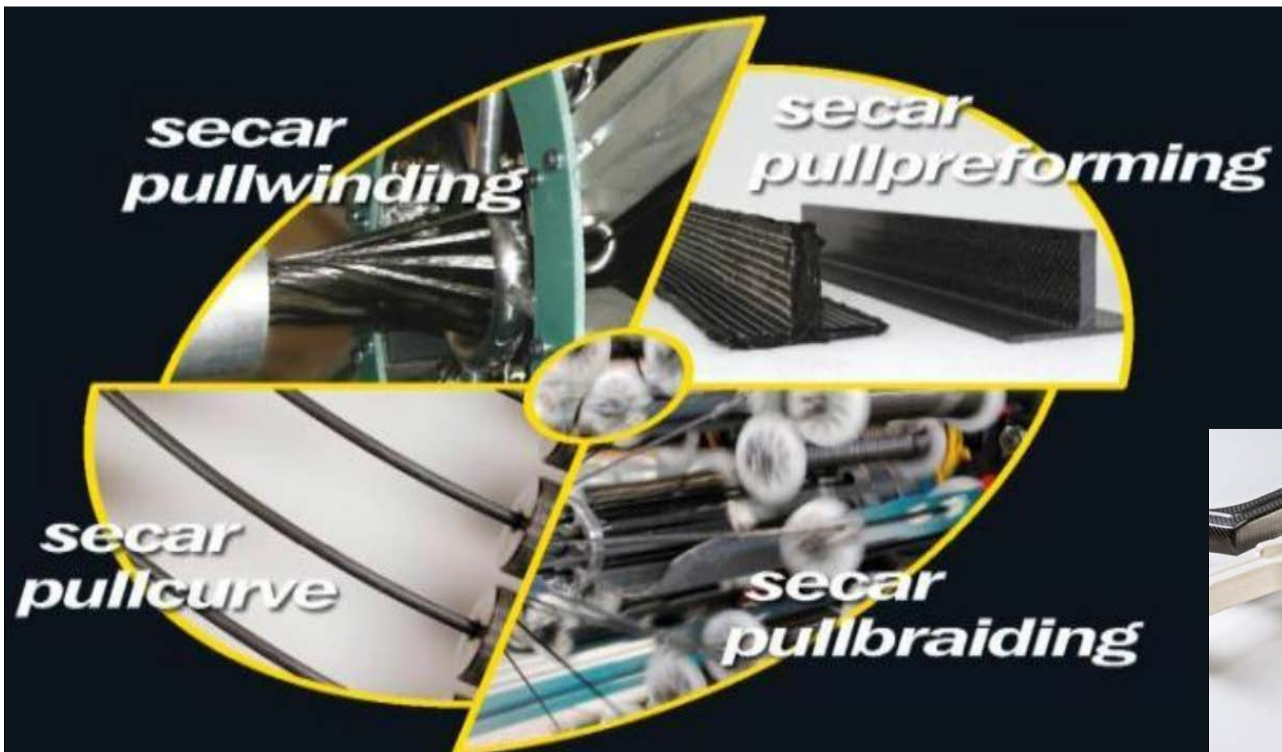
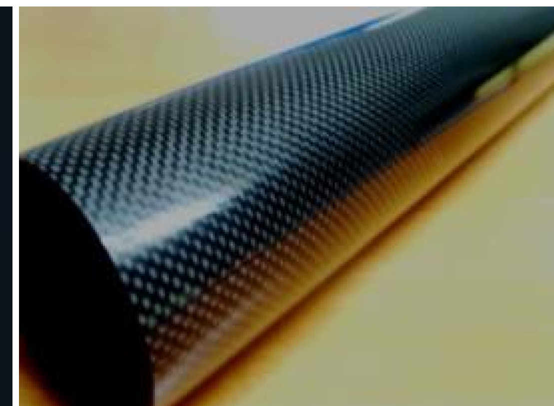
Contents

Contents

Carbon-fibre reinforced polymer composites (CFRP)

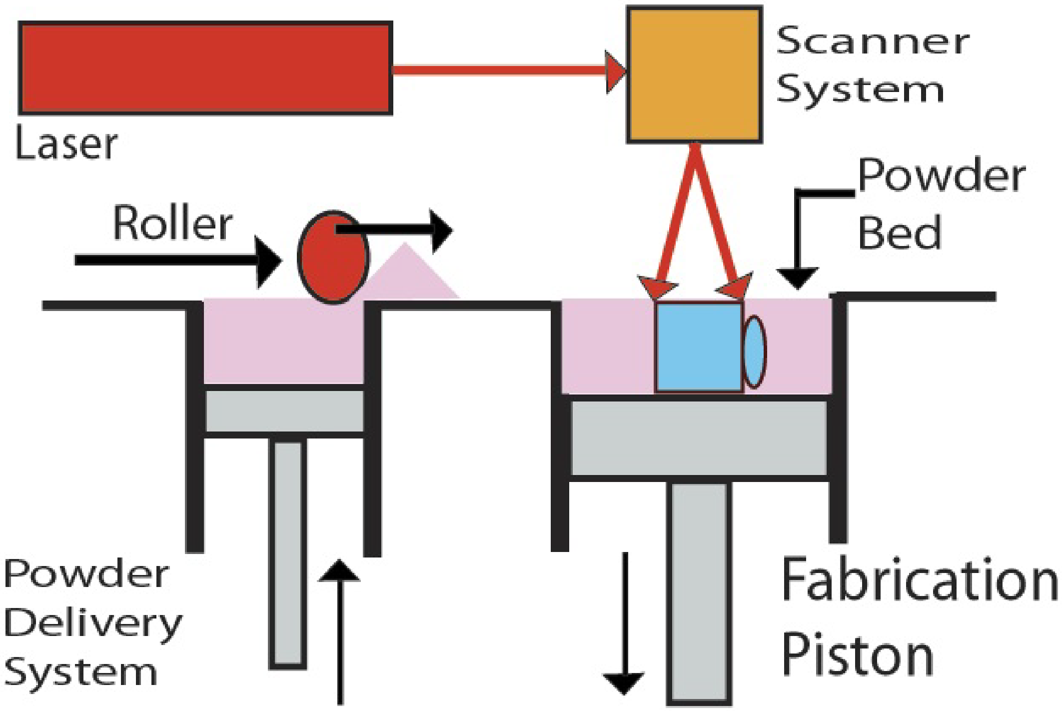
- High specific strength, but low tribological resistance (abrasive / adhesive wear)

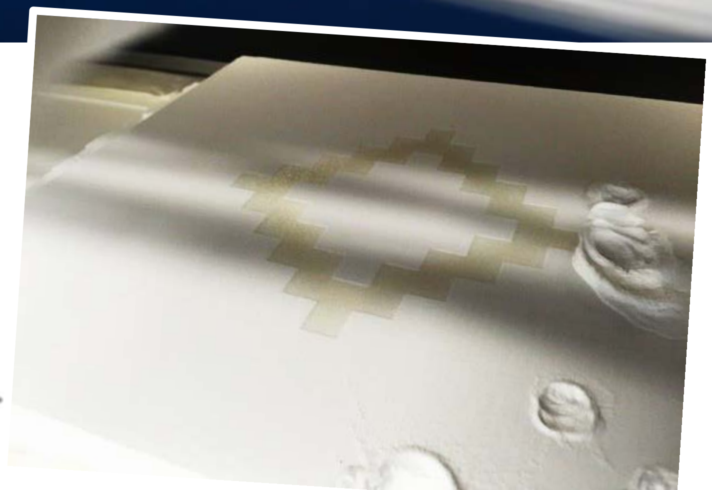




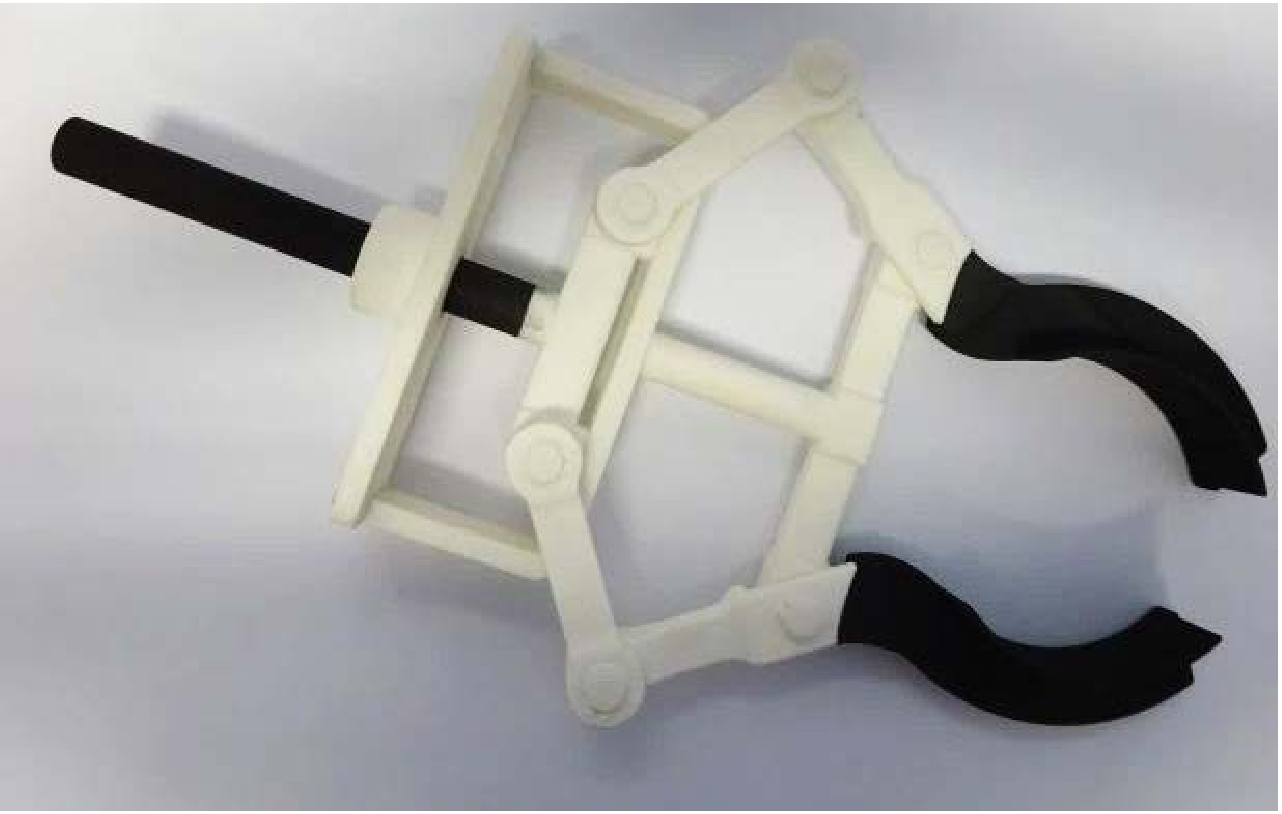
Additive Manufacturing / 3D-Druck

- Selective Laser Sintering (SLS) of PA12





Additive Manufacturing / 3D-Druck



Contents

Polymers and the need for coatings

Polymer materials / plastics

advantages

- Low specific density
- Easy manufacturing

disadvantages

- Low hardness
- Low mechanical strength
- Low temperature resistance

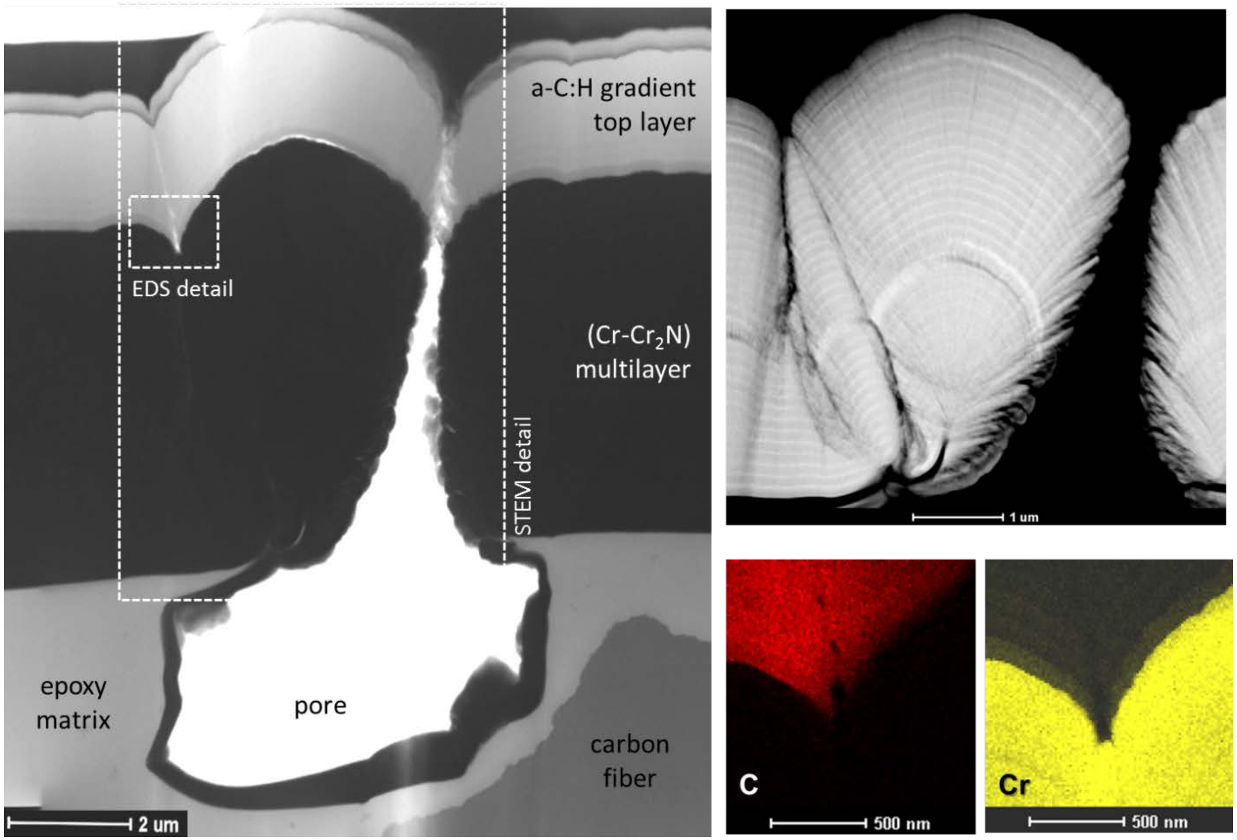
Aim of coating

Increasing the scratch (wear) **resistance**

Functionalization of the surface
(sensoric, optical, decorative, biocompatible properties)

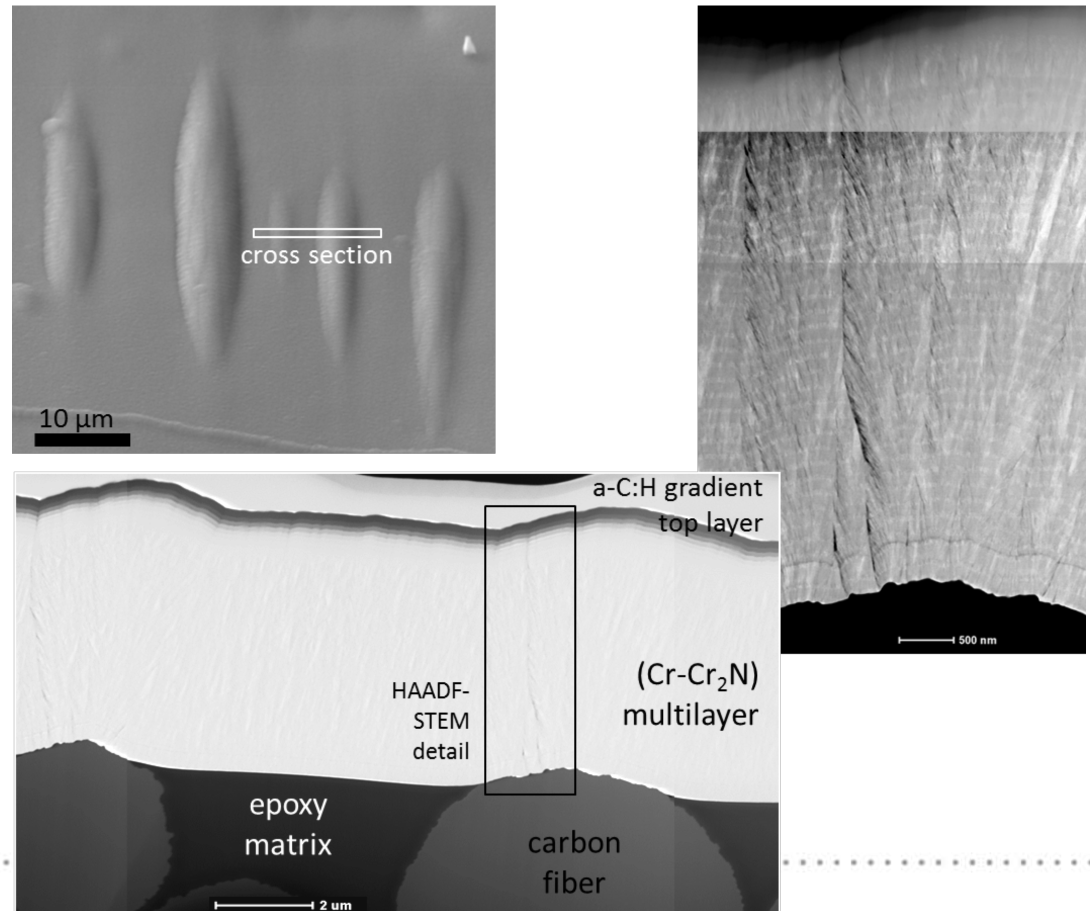
Defects on CFRP surfaces and in coatings on CFRP

- Pores in substrate surface



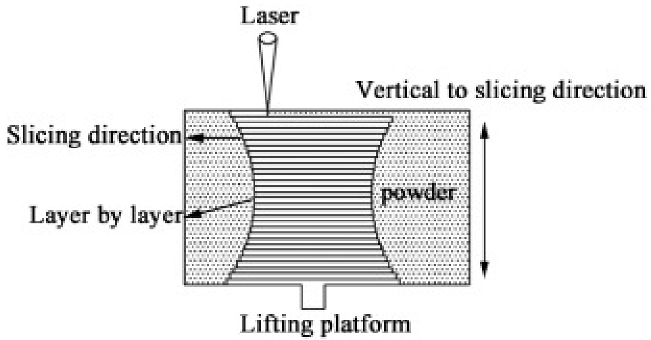
Defects on CFRP surfaces and in coatings on CFRP

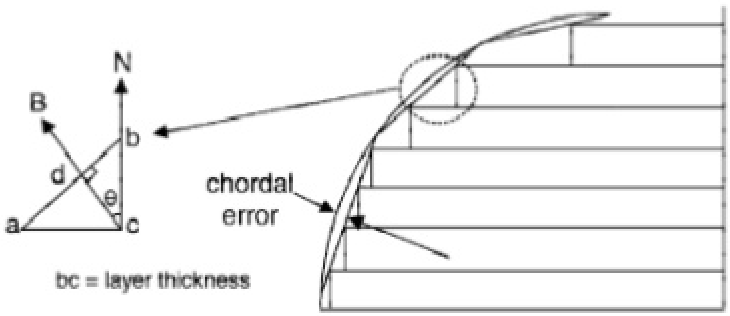
- Surface roughness – carbon fibres protuding epoxy surface



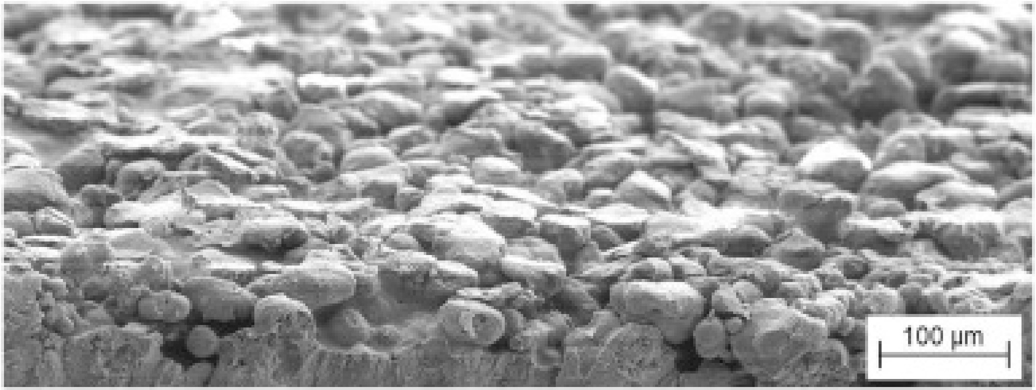
Defects on 3D-printed SLS surfaces

- Waviness – stair stepping





- Roughness – weakly sintered powder



Demands for coatings

Key factors in polymer coating:

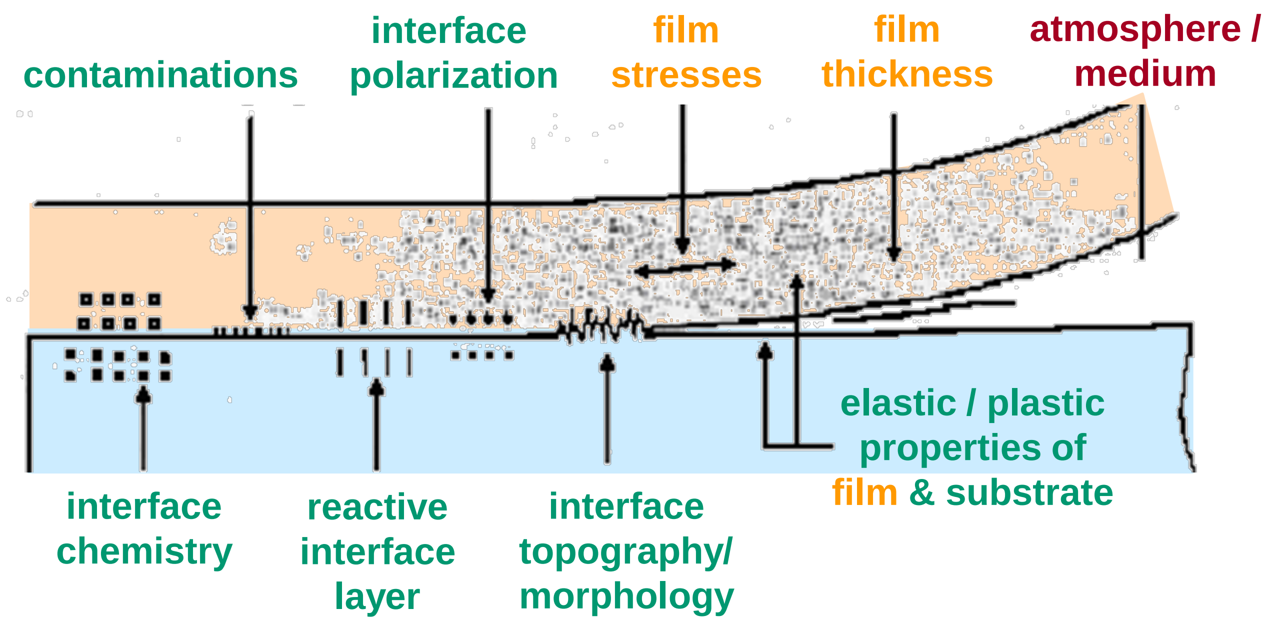
- **Bridging** the very different **properties** (thermal, mechanical) **between** metal / ceramic **coatings and polymer / composite**
- **Tolerance** to **surface defects**

Further demands:

- Low temperature deposition process – preventing thermal stresses
- Tough coatings with high adhesion and cohesion
- Reduction of film growth stresses
- Load supporting layers to prevent large substrate deflection under loads
- Control of plasma impact on polymer surfaces (degradation, cross-linking)
- Coating materials with low impact of contamination due to polymer degasing in vacuum
- Low friction and wear against various counterparts (dry and lubricated)

Demands on coatings - influences

Adhesion strength:



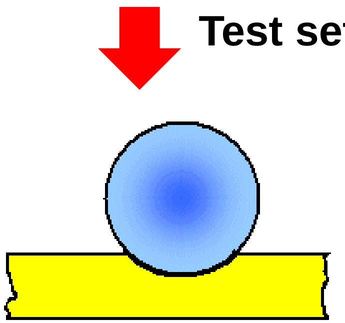
Cohesion strength:

- film density & porosity (deposition technique, energy in plasma / diffusion activation on surface)
- toughness of film material

Contents

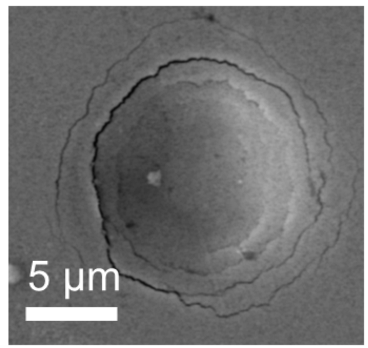
Deformation of hard coatings – brittle single layer TiN

Test setup:

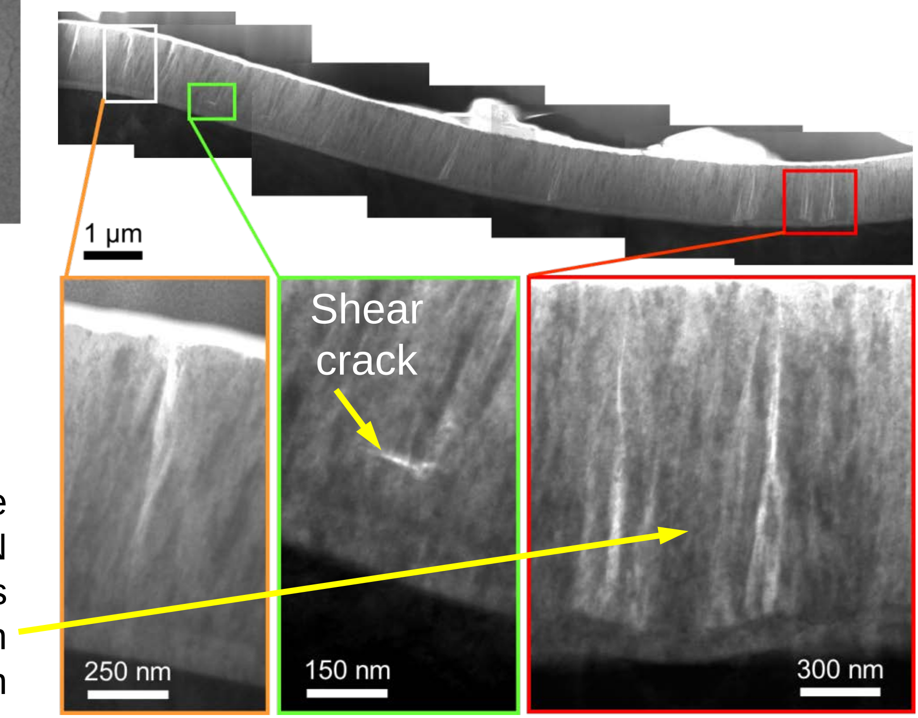


Indentation (max. 0.5 N) by cone-shaped diamond indenter (20 µm tip radius)

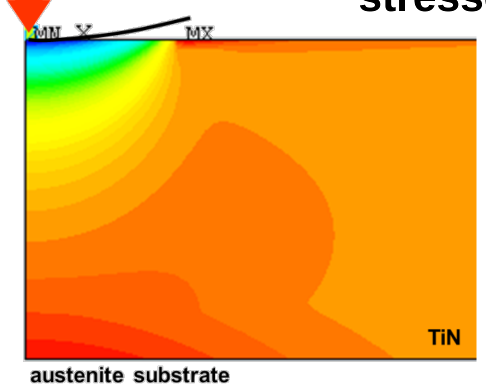
Top view of indent:



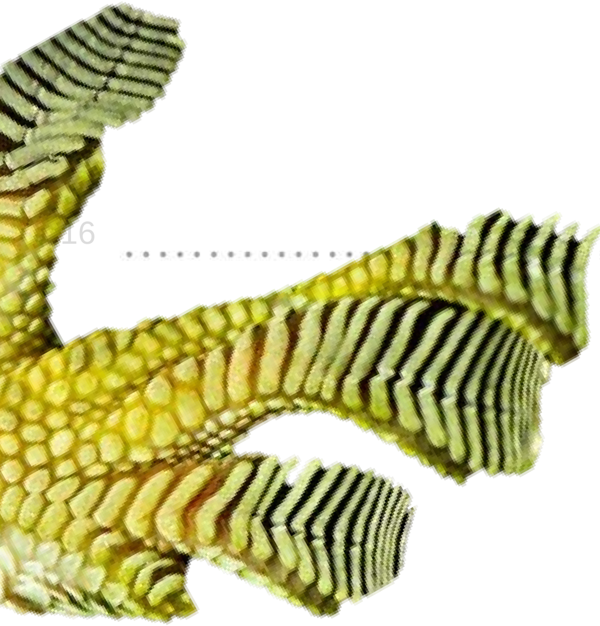
Cross-section view:



FE simulation of von-Mises stresses:



Penetration of tensile cracks in brittle TiN dependent on stress distribution. Cracks run along column boundaries



Biomimetics

=

Study and simulation of biological systems with desired properties

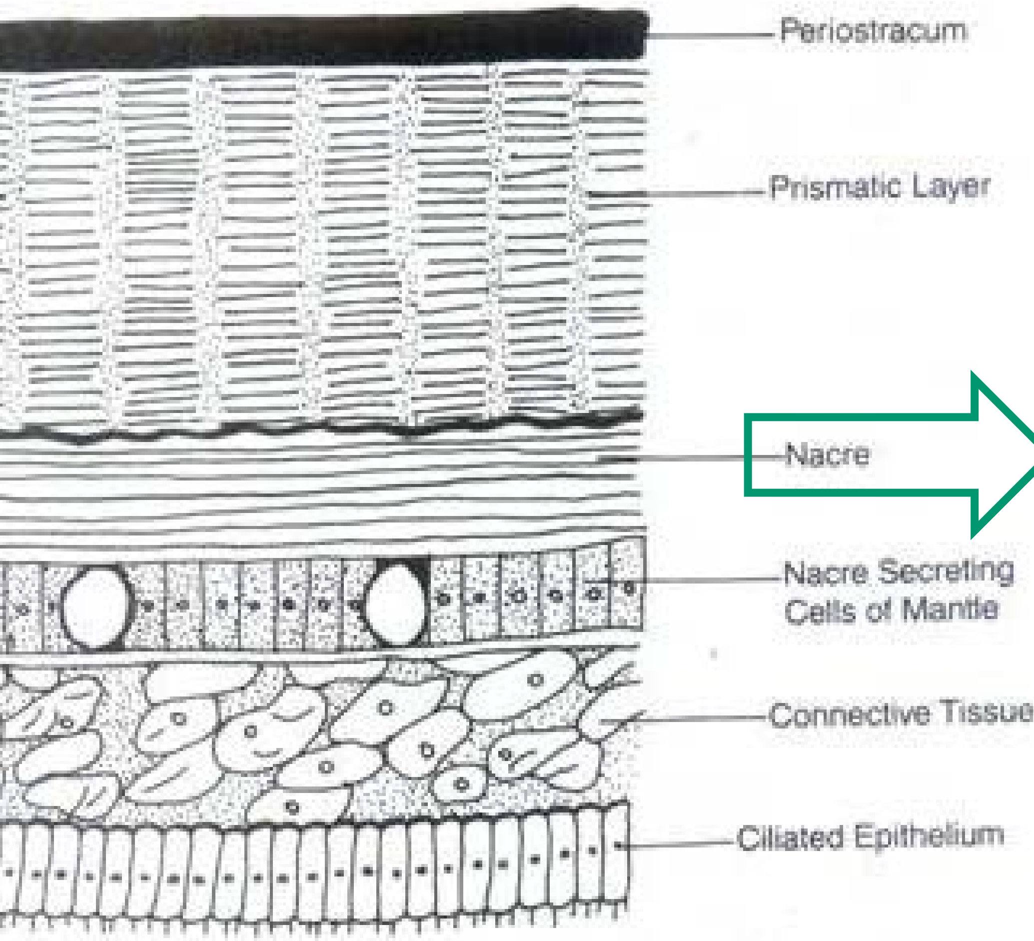
+

Transformation of the underlying principles **into man-made technology**

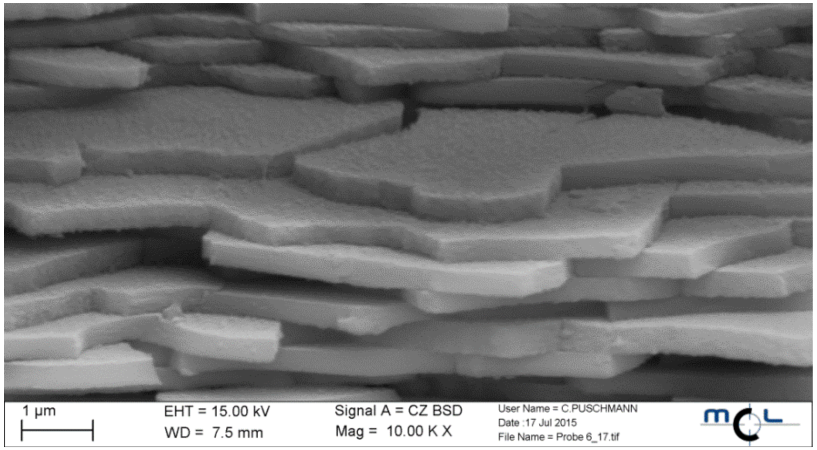
Mimicking nacre deformation by soft-hard multilayer coatings

Biological antetype:
Nacre of molluscs

Microstructure of shells



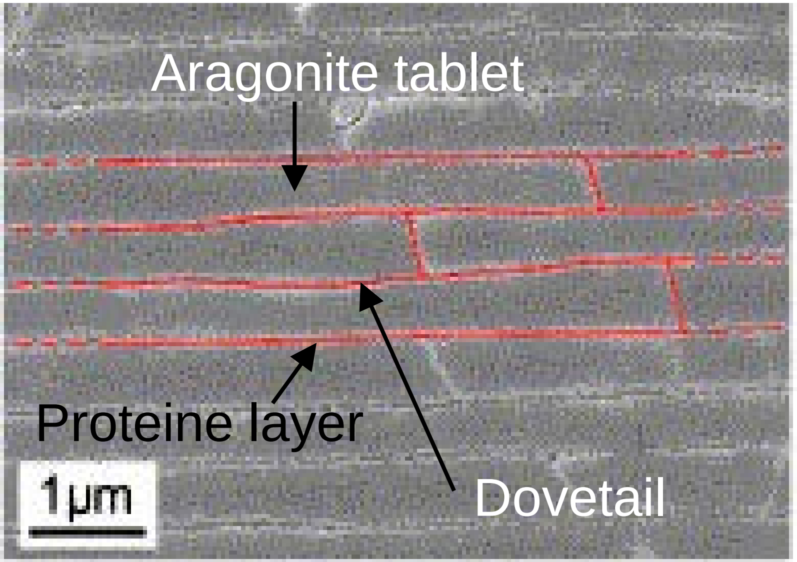
- **Structure of nacre**



- 95% aragonite ($CaCO_3$) tablets with 5% soft organic phase (proteins and polysaccharides)
- 3D wall or columnar structure dependent on mollusc shell species

Mimicking nacre deformation by soft-hard multilayer coatings

Deformation of nacre



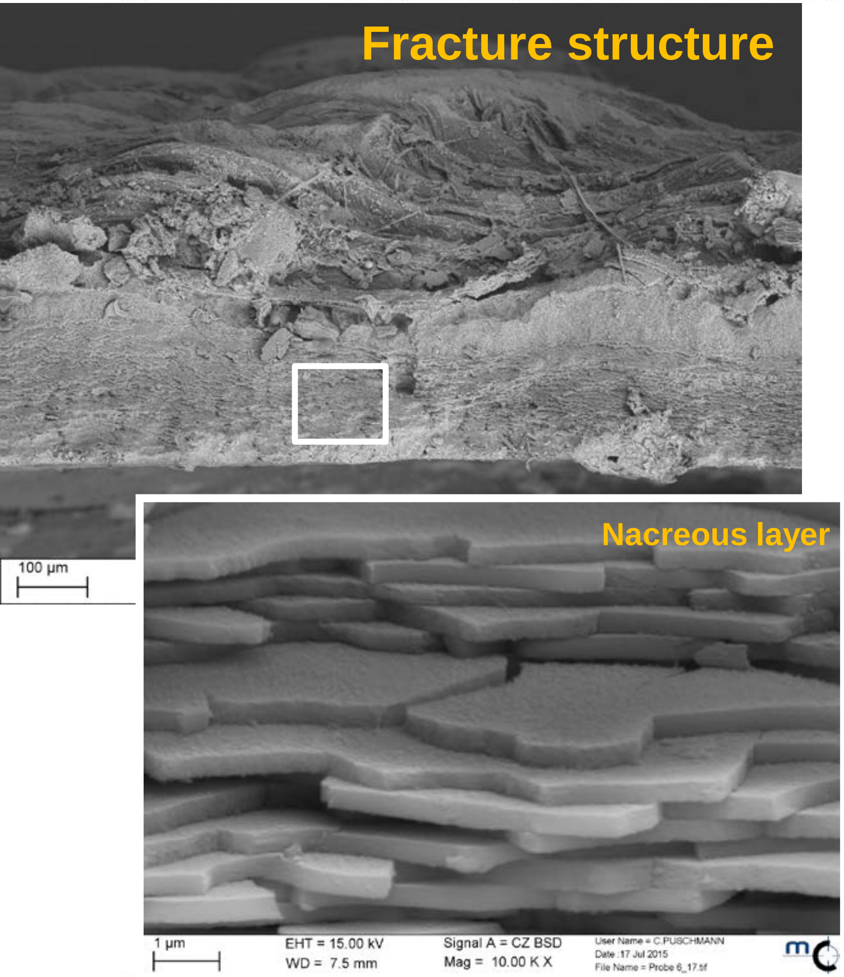
- Minimal impact by nanostructure of $CaCO_3$ tablets
- Huge effect of organic phase – maintains the cohesion of tablets over large separation distances (uncoiling of modules)
- Nanoasperities on tablets provide frictional resistance to sliding
- „Dovetail“-like waviness of tablets (~ half to one tablet length with amplitude ~¼ thickness) act as interlocking-based hardening mechanism during sliding
- **Effect: Extremly high toughness combined with high hardness**

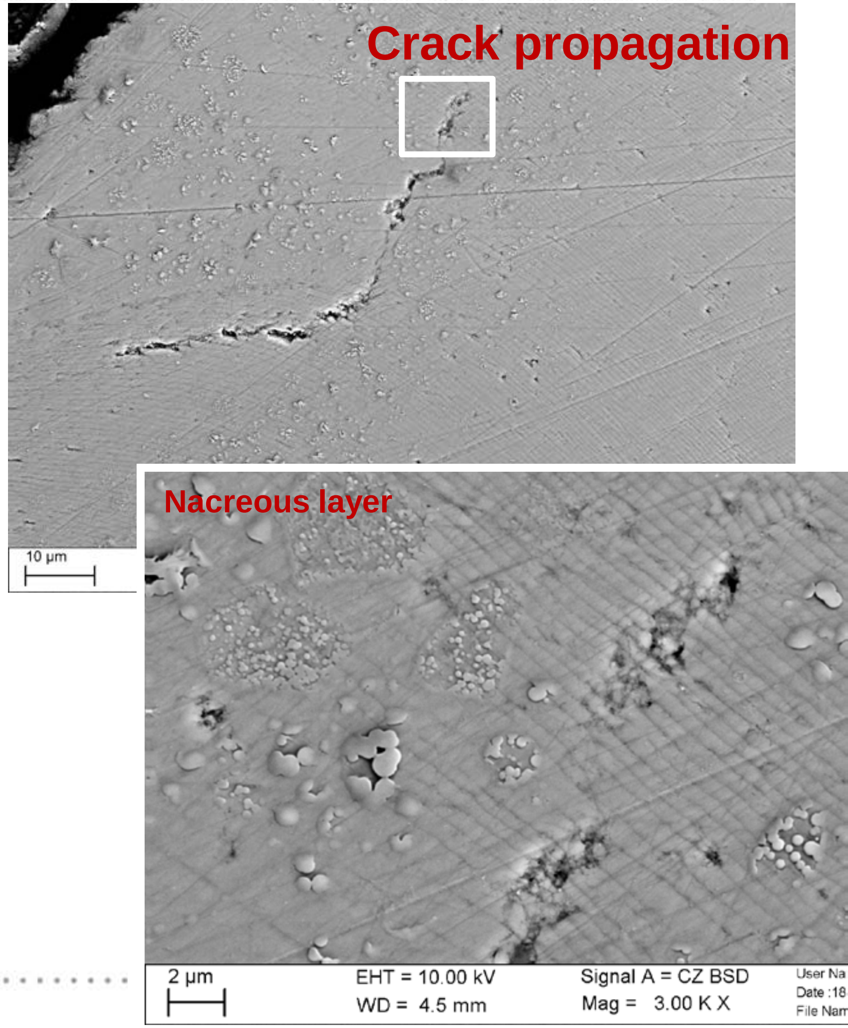
F. Barthelat, C.M. Li, C. Comi, H.D. Espinosa, J. Mater. Res. 21 (2006) 1977.
A.P. Jackson, J.F.V. Vincent, R.M. Turner, Proc. R. Soc. London 234 (1988) 415.
B.L. Smith, T.E. Schaffer, M. Viani, J.B. Thompson, N.A. Frederick, J. Kindt, Nature 399 (1999) 761.
R.Z. Wang, Z. Suo, A. G. Evans, N. Yao, I. A. Aksay, J. Mater. Res. 16 (2001) 2485.
F. Barthelat, H. Tang, P.D. Zavattieri, C.M. Li, H.D. Espinosa, J. Mech. Phys. Solids 55 (2007) 225.

JOANNEUM RESEARCH MATERIALS

Biomimetic archetypes

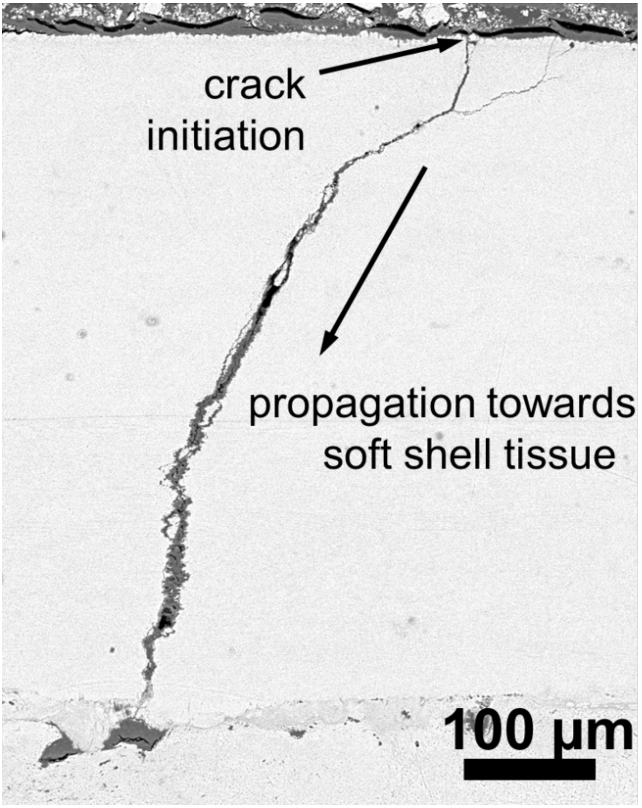
Haliotis discus hannoi

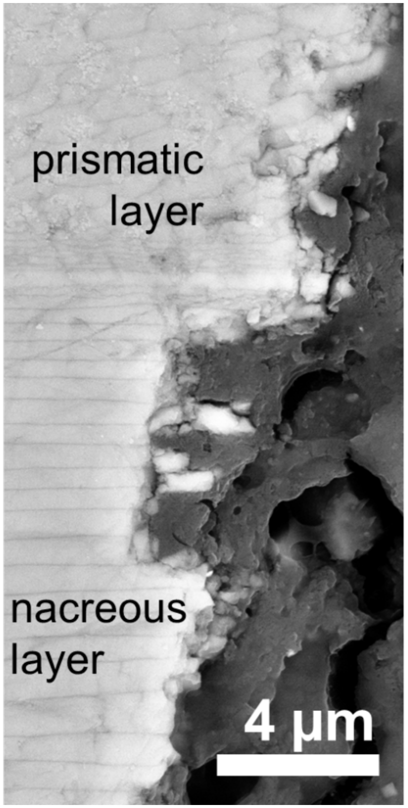


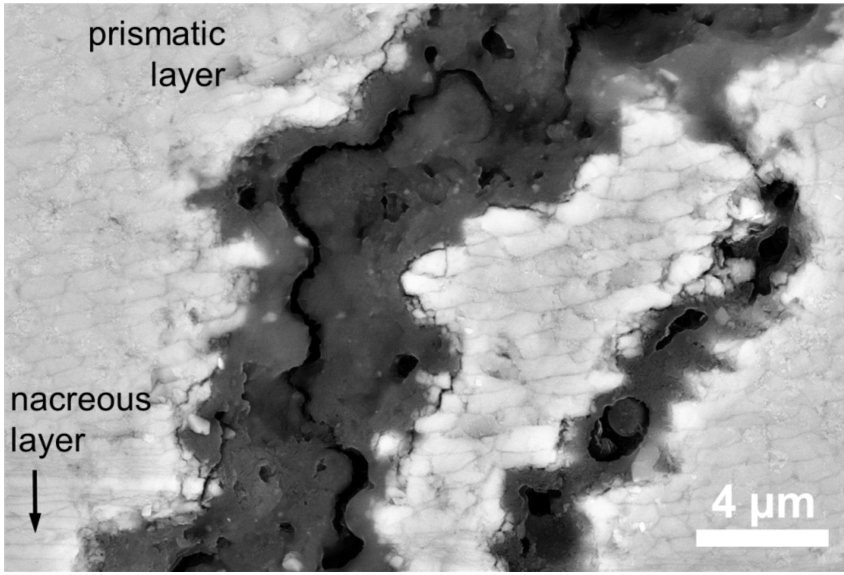


Biomimetic archetypes

Mytilus edulis

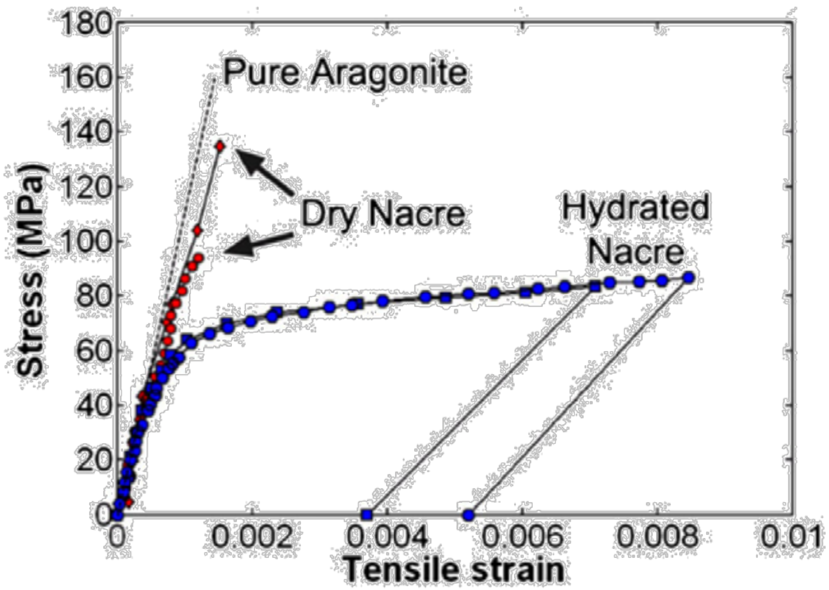


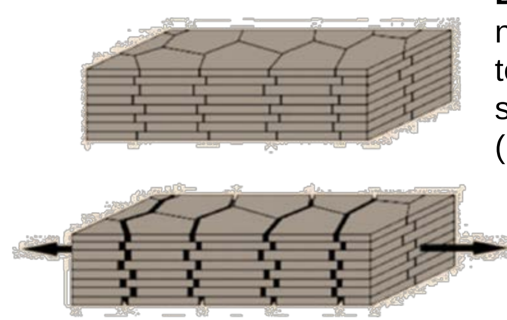




Mimicking nacre deformation by soft-hard multilayer coatings

Deformation of nacre





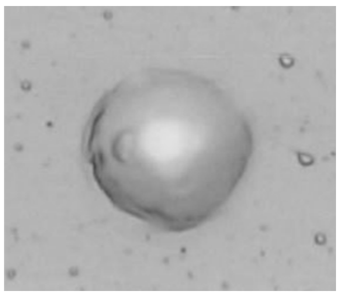
Ductile behavior of hydrated nacre by load transmission by tensile stressing of tablets and shear stressing of interfaces (protein layer)

Failure: large shearing at interfaces (pull-out of tablets)

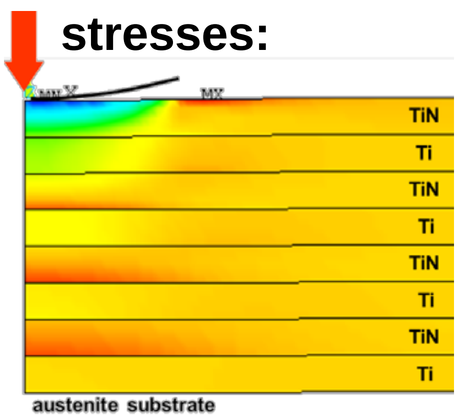
H.S. Gupta, J. Seto, W. Wagermaier, Proc. Natl Acad. Sci. USA 103 (2006) 17741.
M.F. Doerner, W.D. Nix, J. Mater. Res. 1 (1986) 601.

Deformation & fracture of hard coatings – tough multilayer Ti-TiN with defect-tolerance

Top view of indent:

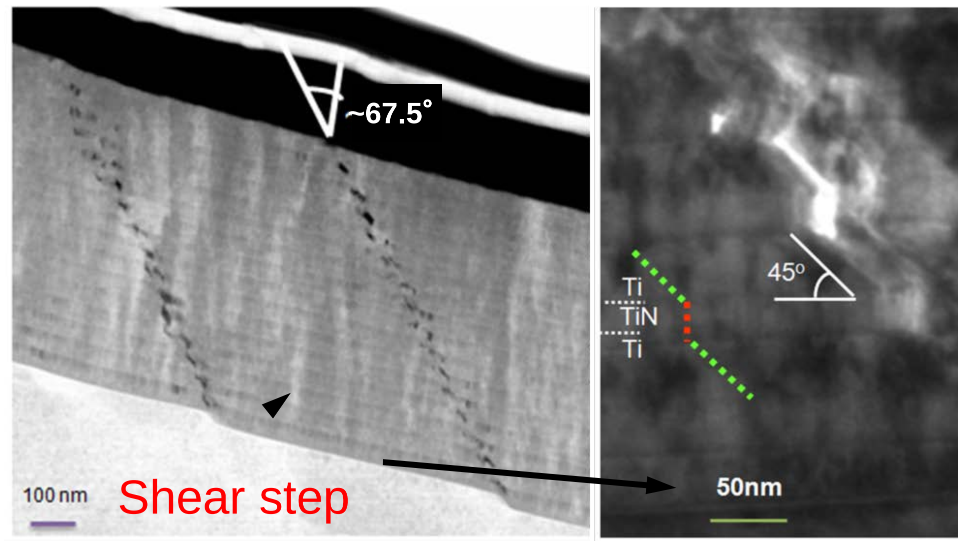


FE simulation of von-Mises stresses:

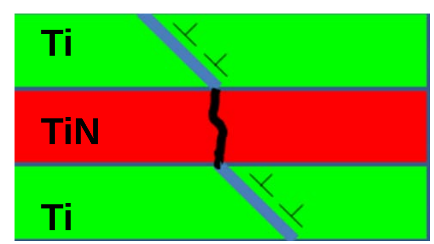


Stresses lower at same loading

Cross-section view:



No total coating failure



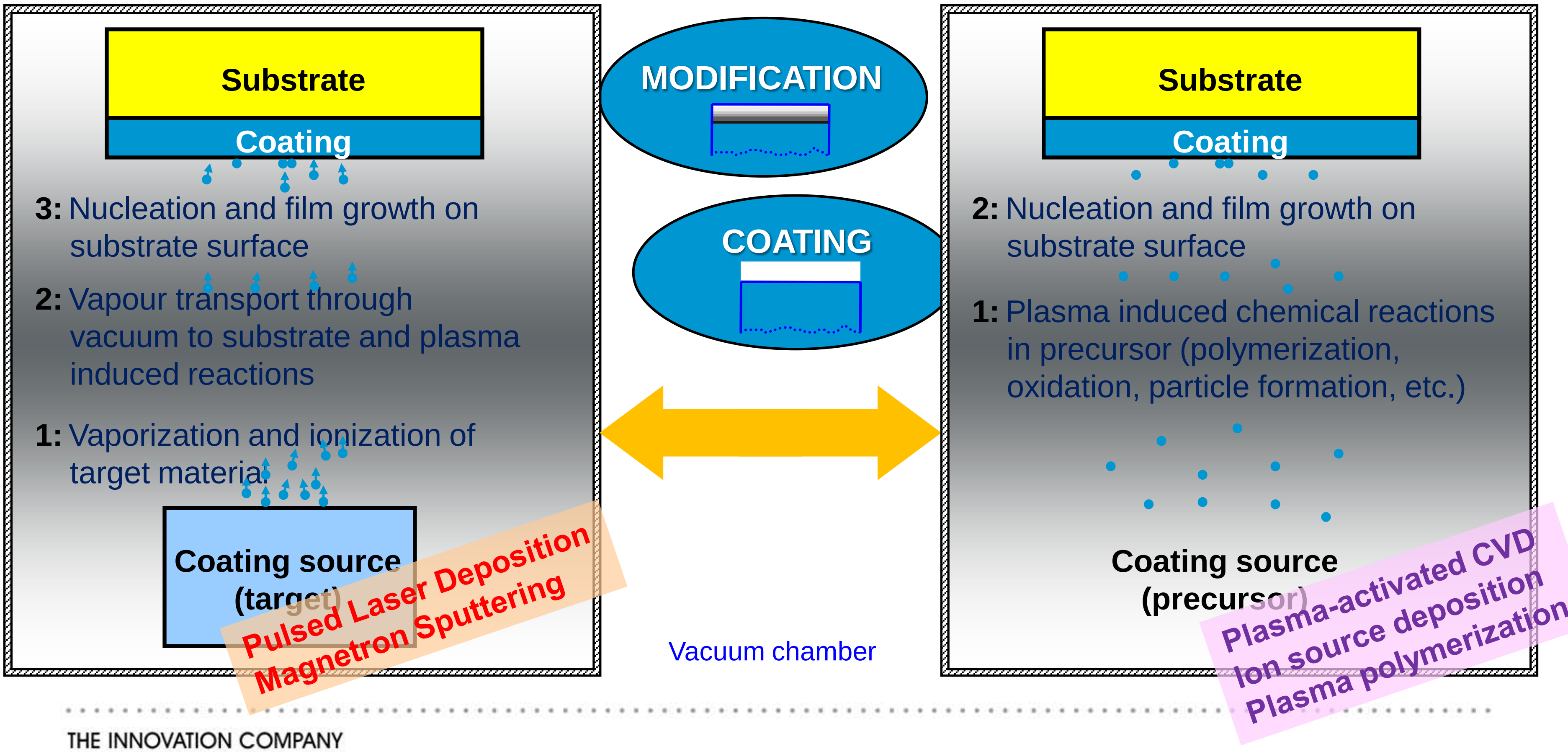
Shearing in metal Ti layers (45° to normal force)

Brittle fracture in TiN

Contents

Our approach –
Methods of plasma-based coating deposition

- **Physical vapour deposition (PVD)**
- **Chemical vapour deposition (CVD)**



Low-vacuum deposition processes

Plasmapolymerization (PP)

Hybrid (PP + Atomic Layer Deposition)

Plasma-assisted chemical vapour deposition

- Capacitive coupled plasma
  - Frequency: 40 kHz
  - Power: up to 3000 W
- Usable chamber volume: planetary diameter 300 mm, height 630 mm
- Gases: Ar, O_2, N_2, C_2H_2, SF_6, HMDSO, HMDS, CF_3H, etc.
- Gas pressure: 5 x 10^{-2} to 2.5 mbar

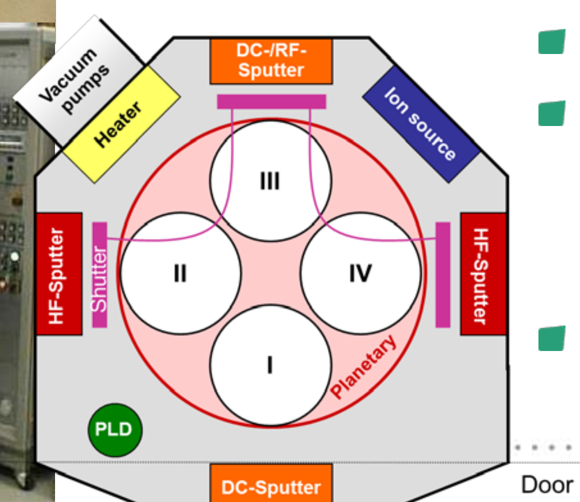
High-vacuum deposition processes

Pulsed Laser Deposition (PLD)

Magnetron sputtering (MS)

Anode Layer Ion Source treatment and assisted deposition (ALS)

- PLD: KrF & Nd:YAG multi-beam evaporator
- MS: DC, DC-pulsed, RF on 1-4 sputter magnetrons



- ALS: Veeco ALS 340
- Usable chamber volume: planetary diameter 560 mm, 450 mm
- Gas pressure: 10^{-4} to 10^{-2} mbar

Contents

Coating architectures / concepts

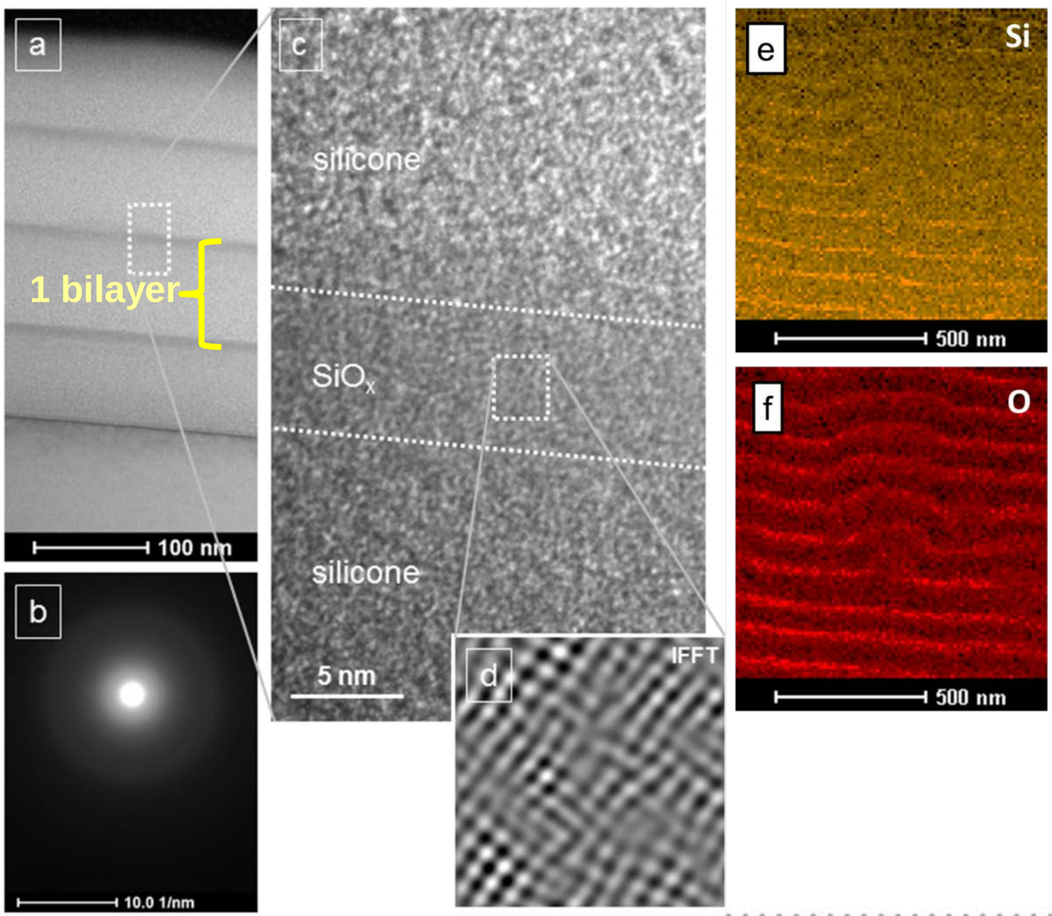
Ultra-low friction top layer

Tribological functional intermediate layer coating

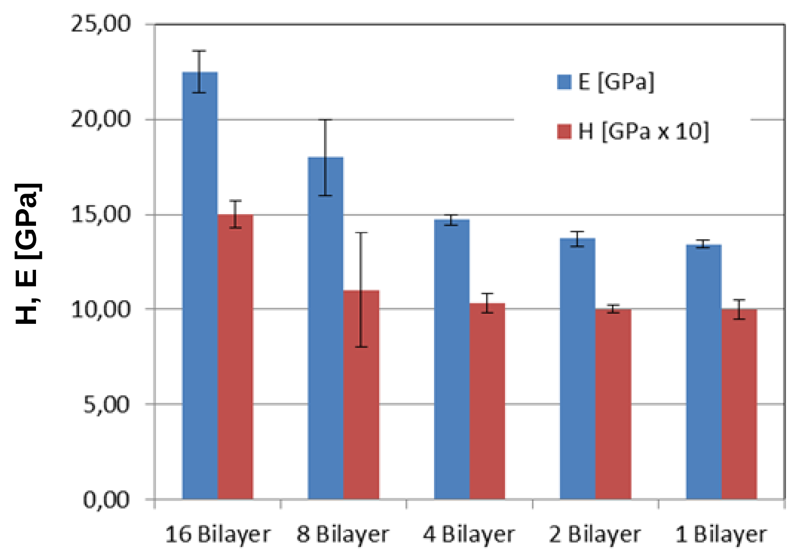
Load support layer
(Cr-CrN_x multilayer coating)

(Carbon-fibre reinforced) polymer substrate

Low-vacuum deposition processes
Coatings‘ microstructure & micromechanics



Coating	Thickness of a bilayer	Total coating thickness
1 bilayer	3950 nm (~4 µm)	3900 nm
2 bilayer	1963 nm (~2 µm)	3926 nm
4 bilayer	1013 nm (~1 µm)	4052 nm
8 bilayer	521 nm (~0.5 µm)	4168 nm
16 bilayer	248 nm (~0.25 µm)	3968 nm

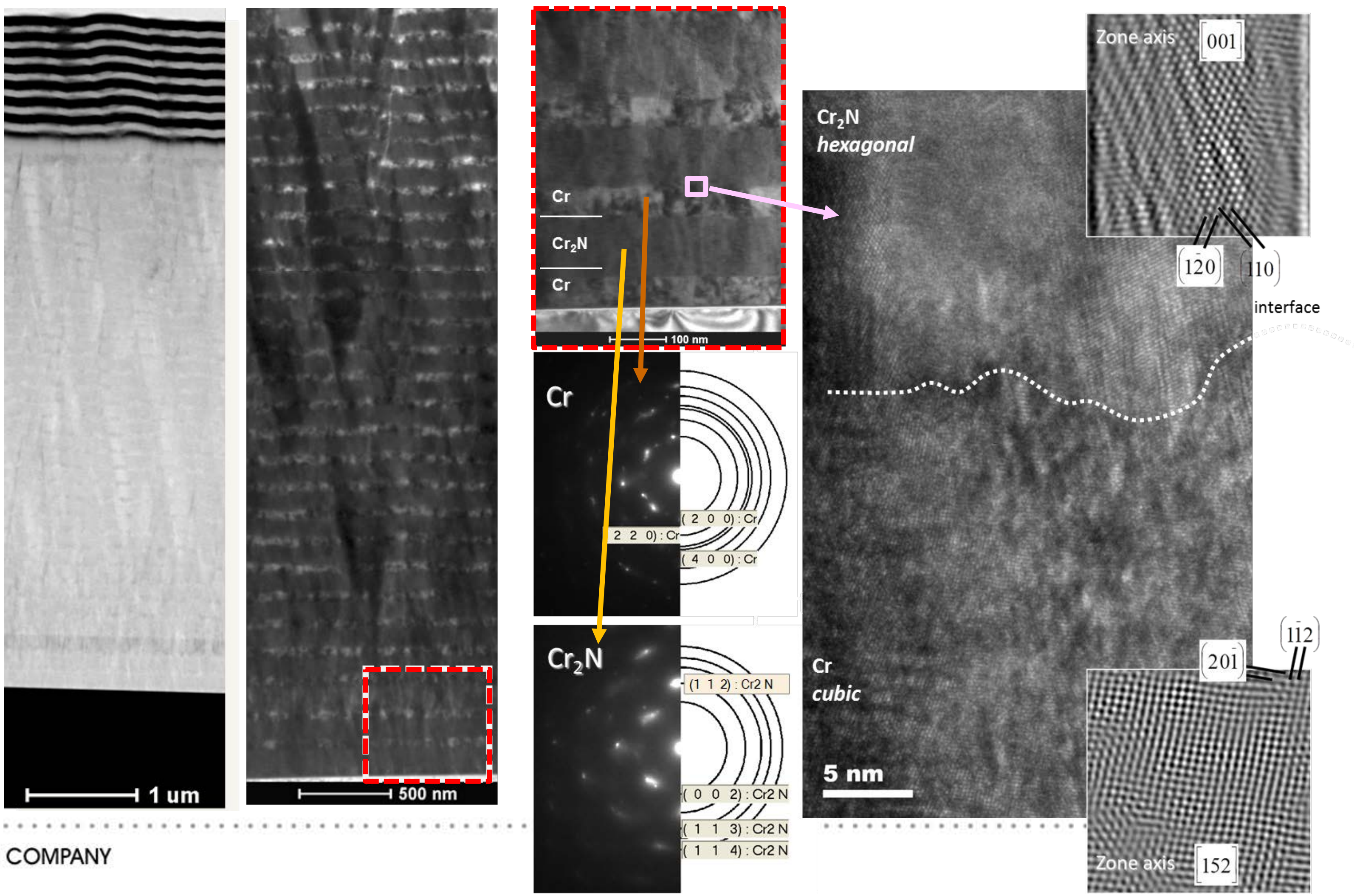


High-vacuum deposition processes $Cr\text{-}CrN_x$ load support base layer

Tribological functional intermediate layer coating

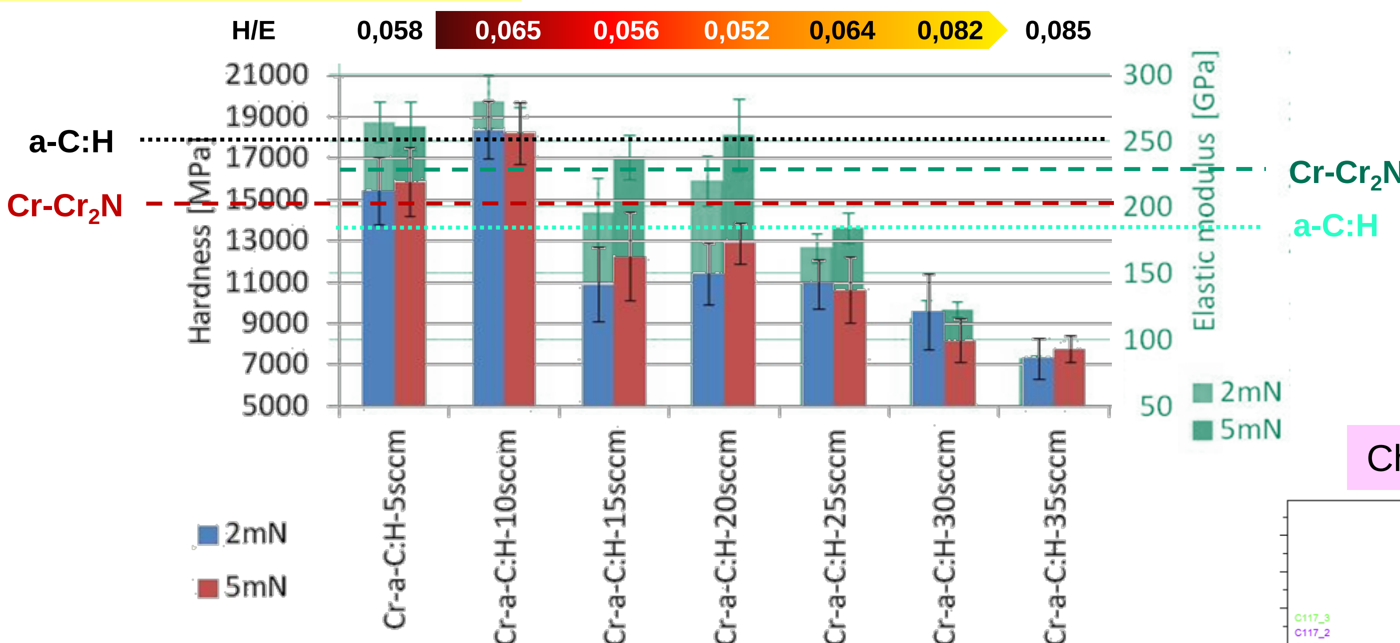
Load support layer ($Cr\text{-}CrN_x$ multilayer coating)

(Carbon-fibre reinforced) polymer substrate



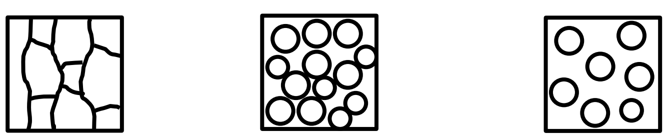
Tribological functional intermediate layer Nanocomposite a-C:H:Cr

Micromechanical properties:



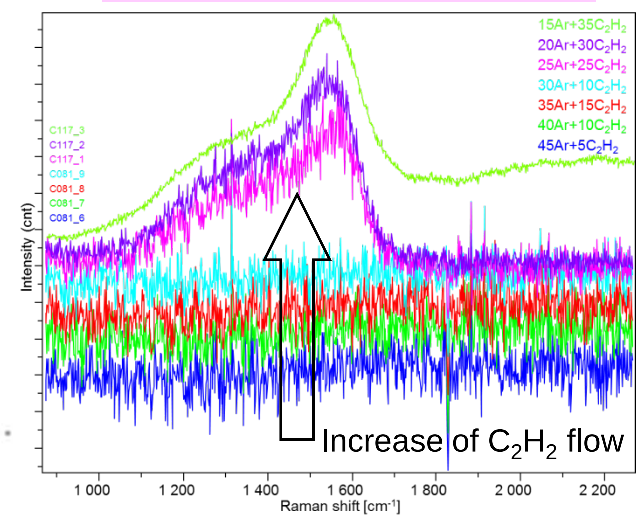
Magnetron sputtering from Cr targets in C_2H_2-Ar atmosphere

Nanocomposite formation:



CrC_x dominance | **CrC_x with small amount of a-C:H matrix** | **CrC_x grains in a-C:H matrix**

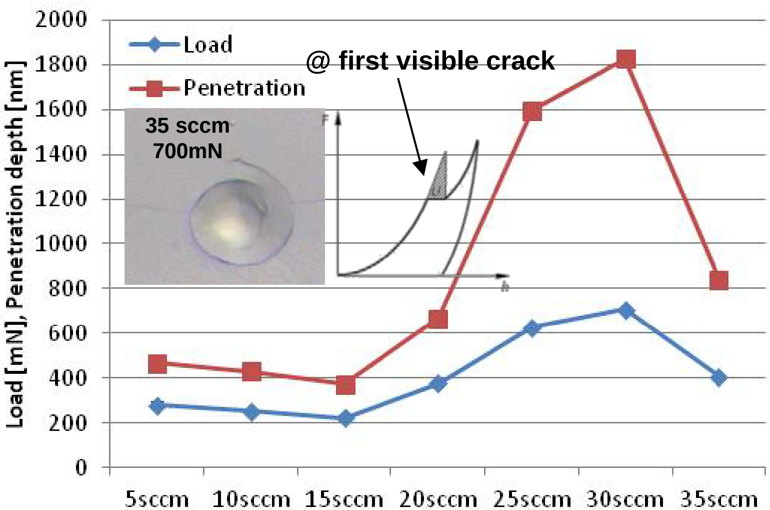
Chemical binding (Raman):



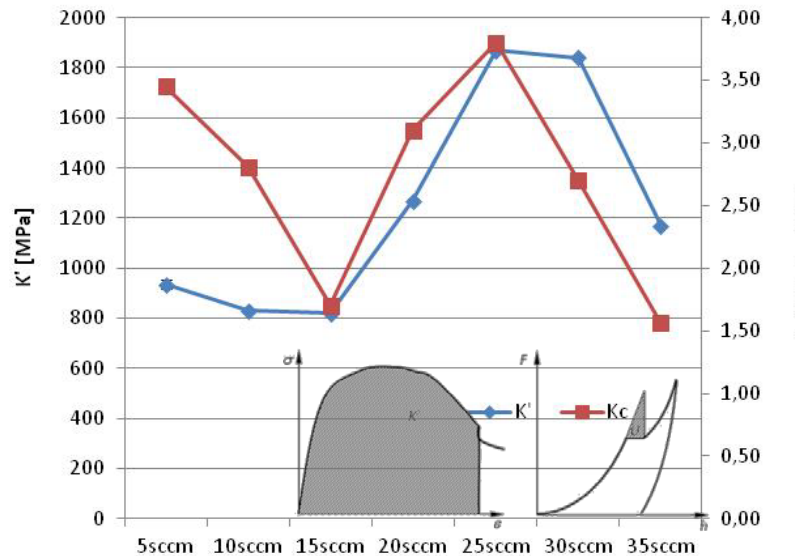
Tribological functional intermediate layer Nanocomposite a-C:H:Cr

1 µm on 4 µm Cr-CrN load support coating

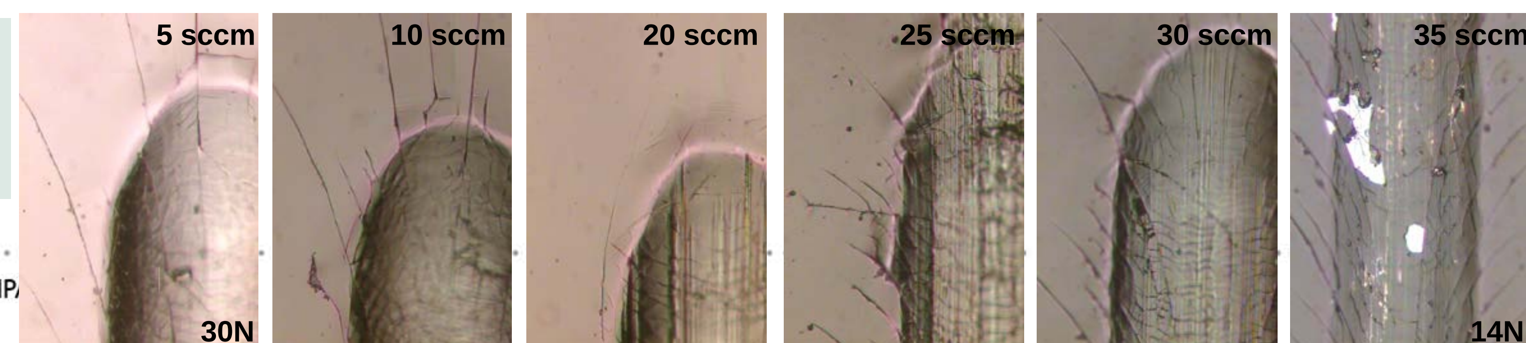
Fracture analysis:
Spherical indentation R100 µm diamond



Toughness calculated from indentation curves and stress-strain curves:



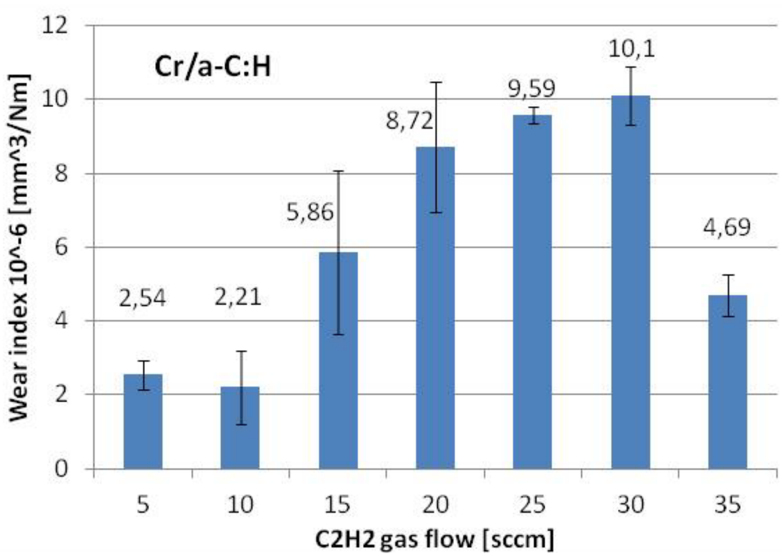
Scratch test:
(100 µm HRC tip) @ maximum load of instrument (30 N)

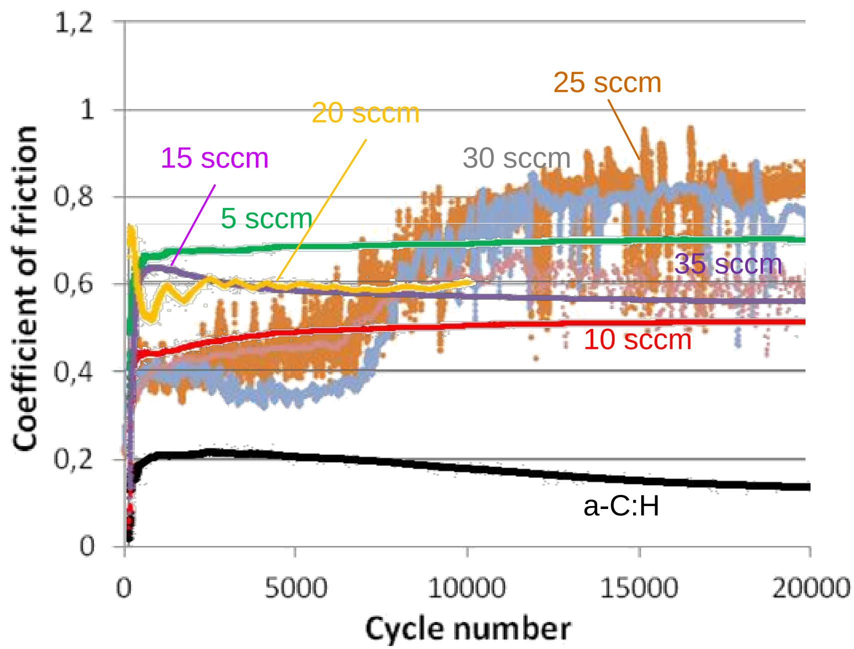


Tribological functional intermediate layer
Nanocomposite a-C:H:Cr

1 µm on 4 µm Cr-CrN load support coating

Ball-on-disc test:
Al_2O_3 ball, 6mm, F_N=1N, 20.000 cycles, 0,06m/s speed, Hertzian pressure σ_H=0,36 GPa



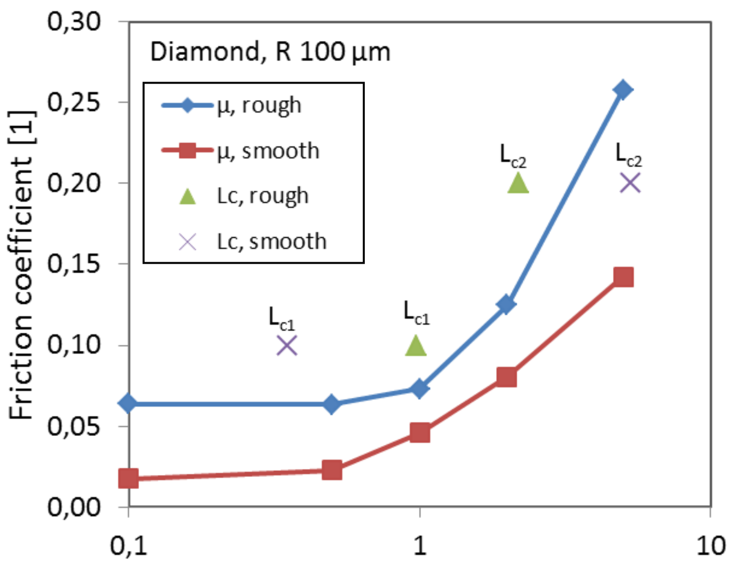


Low friction behaviour achieveable only by a-C:H,
but a-C:H:Cr provides much higher H/E ratio and toughness

Roughness influence

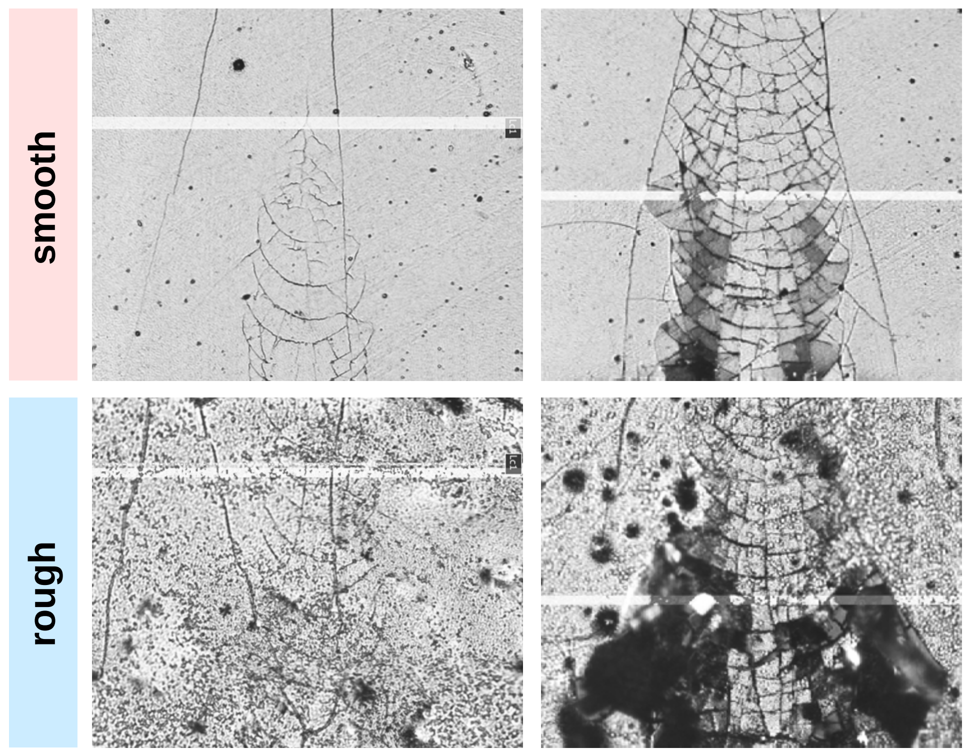
Scratch resistance on CFRP

R100 µm HRC diamond



L_{c1} (COhesive film failure)

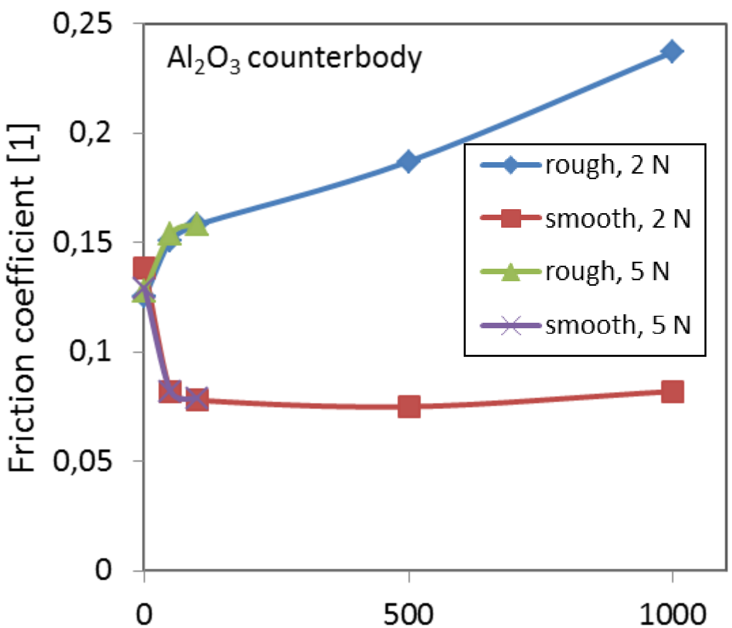
L_{c1} (ADhesive film-substrate delamination failure)

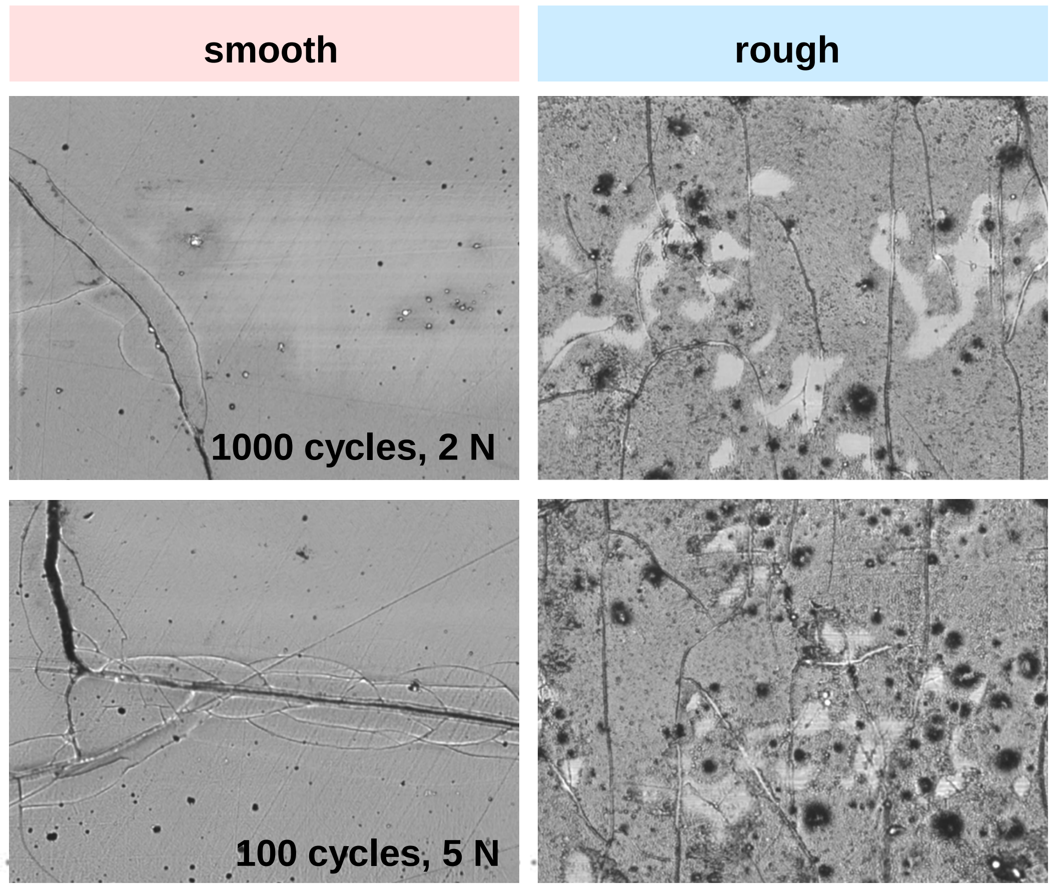


Roughness influence

Reciprocating sliding

D6 mm **Al_2O_3** ball

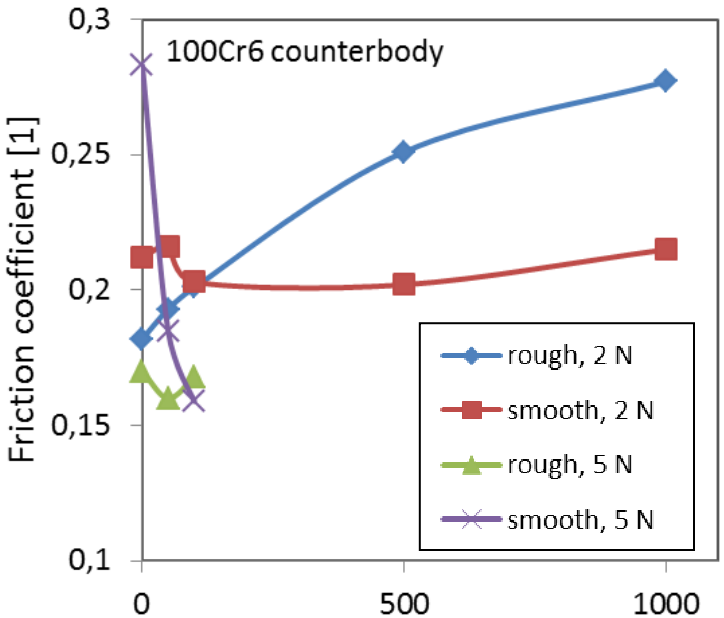


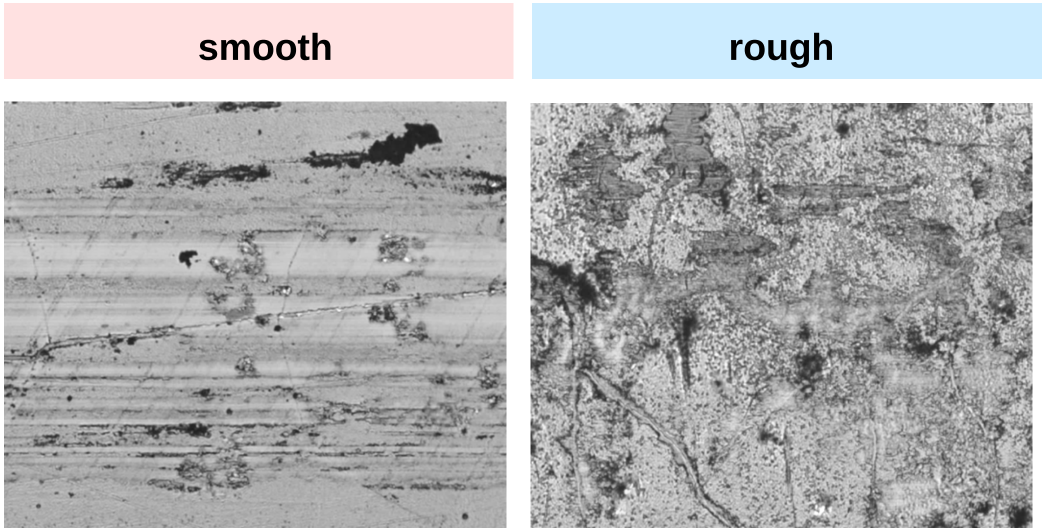


Roughness influence

Reciprocating sliding

D6 mm **100Cr6 steel ball**

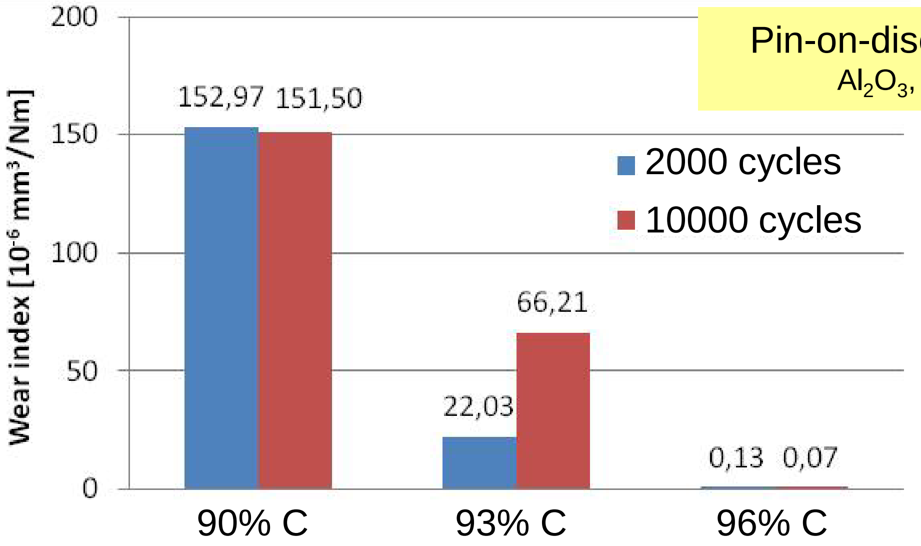


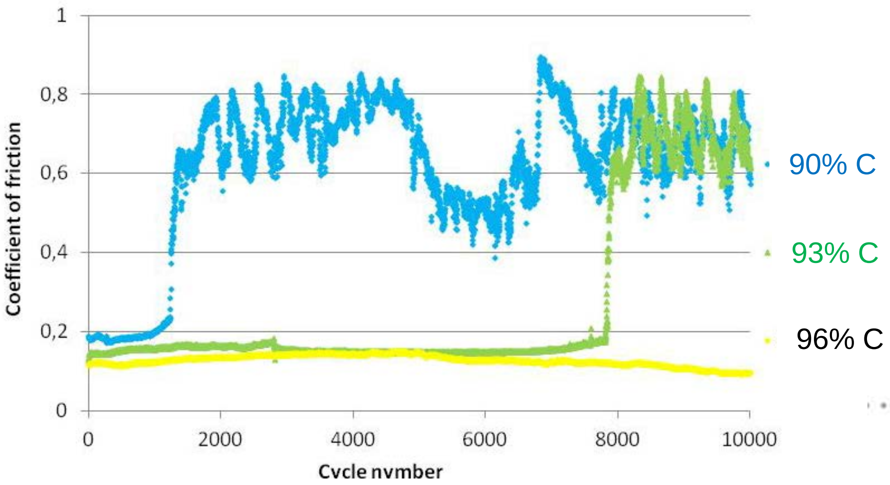


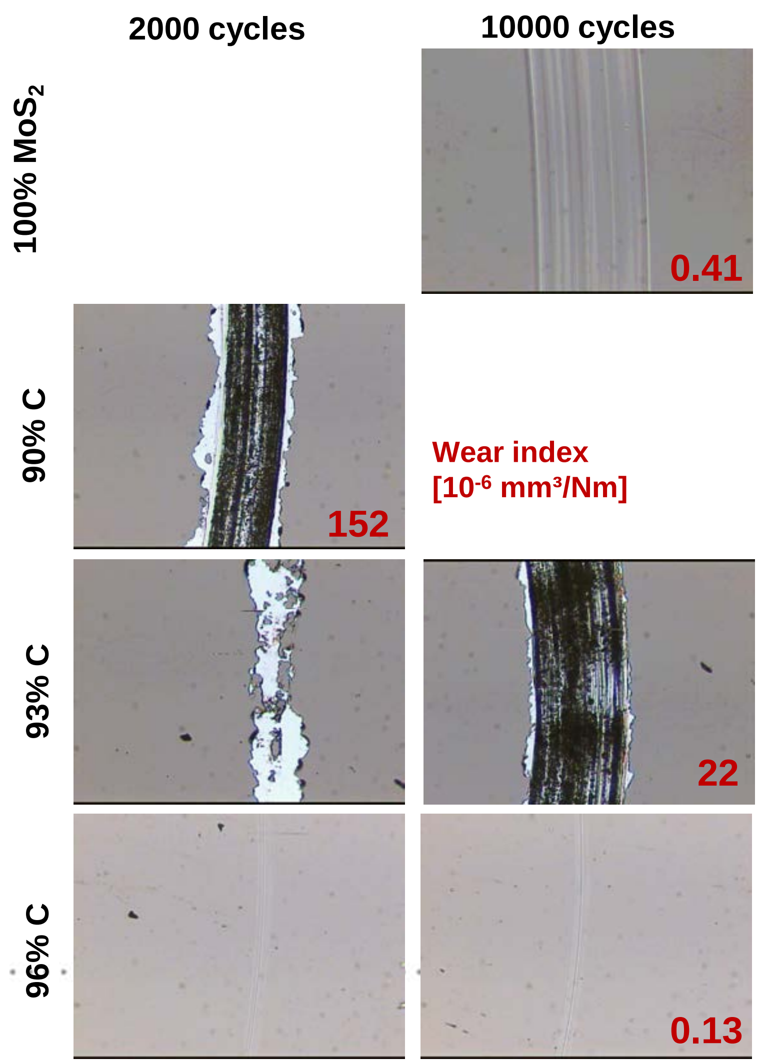
1000 cycles, 2 N

Top layers – Tribological properties of a-C:H(:MoS_2) nanocomposites

Pin-on-disc testing
Al_2O_3, 1 N







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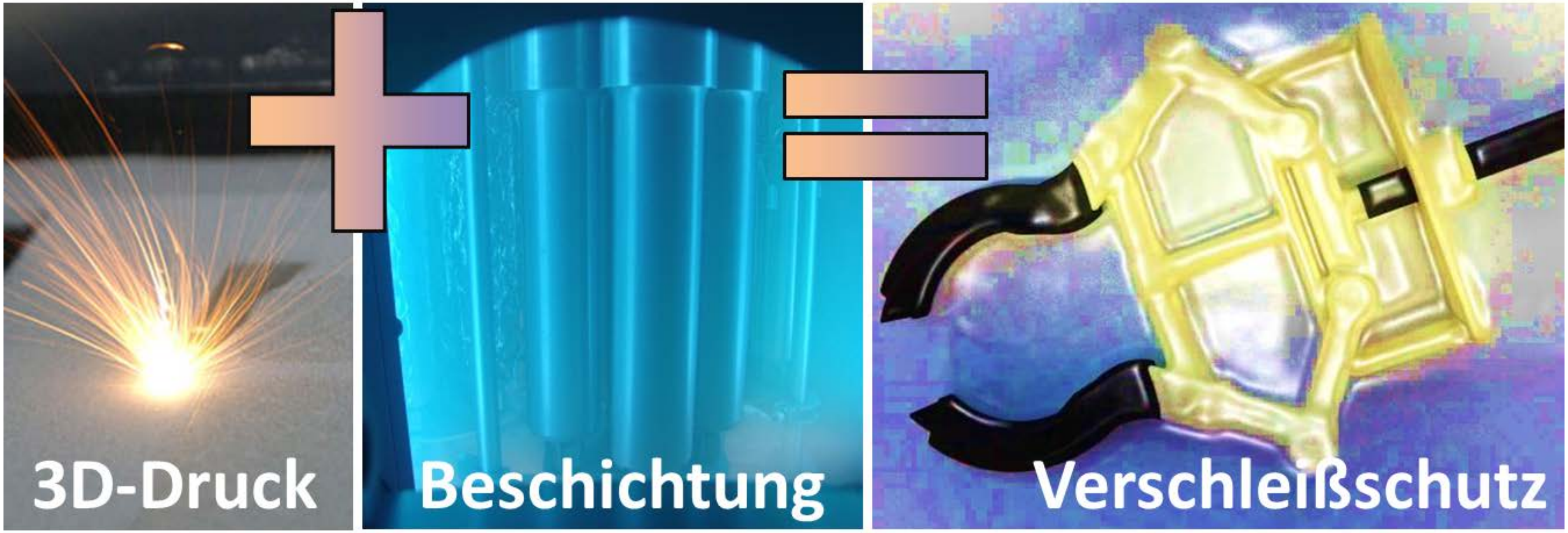
Conclusions



Thanks to project partners

FARSOON TECHNOLOGIES

LSS Additive Manufacturing Solutions

Sony DADC

Invibio® biomaterial solutions

bvt BESCHICHTUNGS-UND VERSCHLEISSTECHNIK

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Veeco

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