Industrial Applications of Hard and Superhard Nanocomposite Coatings for Machining, Injection Molding and the like

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Outline

1. Mechanisms of Hardness Enhancement & Design Concept of Hard & Superhard Nanocomposites
2. Their advantages & drawbacks
3. Selected Examples of their Industrial Applications
4. Conclusions & outlook

THANKS TO
Dr. P. Holubář SHM & Jílek SHM (CZ), Dr. T. Cselle PLATIT AG (CH), Dr. Maritza Veprek-Heijman Dr. R. Tietema Hauzer (NL) and many colleagues from joint research projects

These Nanocomposites are not the “Materials of the Future”
they are already in Many Industrial Applications

The industrial applications of superhard nanocomposites as wear-protection coating on tools for machining have been pioneered by small Czech company SHM (Šumperk) since 1995.

Conventional: TiN, Ti_{1-x}Al_xN, Cr_{1-x}Al_xN, TiC_{1-x}N_x, ...
Nanocomposites: nc-TiN/Si_3N_4, Ti_{1-x}Al_xN/Si_3N_4, ...

For pressurized casting of Al-alloys

Thin top TiN for esthetics

Different colors
Why Coatings on Tools?
Why Coatings on Tools?

- Higher hardness & oxidation resistance of the tool material
- Lower coefficient of friction

Materials of tools:

Cemented Carbide (WC-Co): $H \leq 20$ GPa, poor oxidation resistance
High Speed Steel (HSS): $H \leq 9$ GPa; $T < 530^\circ$C & poor oxidation resistance

Hardness of Coatings (GPa): TiN - 21; TiAlN - 25; Nanocomposites > 40

Oxidation Resistance of Nanocomposites $\geq 900$-1000 $^\circ$C

![Oxidation Rate Graph](chart.png)

Oxidation Rate in air (R. U.)

Temperature ($^\circ$C):

- TiCN
- TiN
- TiAlN
- AlTiN

Hardness of Coatings (GPa):

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- TiAlN - 25
- Nanocomposites > 40
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Brief History

For pressurized casting of Al-alloys

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Different colors
The SHM (CZ) company was established in 1993 and operated by the two owners.


SHM as well as the boys grew up.

Our collaboration with SHM begun in 1996.

2001 SHM & PLATIT → joint venture “PIVOT“ → development of LARC® technology

LARC® Coating Unit $\pi^{80}$ presented Dec. 2002

October 2004
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October 2013 PIVOT → PLATIT s.a.

Strong Collaboration SHM & PLATIT continues and the number of different coating equipments increasing.
High-rate deposition of AlTiN and related coatings with dense morphology by central cylindrical direct current magnetron sputtering

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d Department of Chemistry, Technical University of Munich, 85747 Garching, Germany
The industrial applications of superhard nanocomposites as a wear-protection coating on tools for machining have been pioneered by small Czech company SHM (Šumperk) since 1995.

www.shm-cz.cz

Nowadays
Many companies have the nanocomposites in their program and not only nitrides-based ones but also Dimond-Like-Carbon (DLC) – based nanocomposites e.g. company Hauzer (NL)

→ Only Selected Examples on DLC
→ But many typical examples for nanocomposites
**Graphite, Diamond and Diamond-Like Carbon (“DLC”)**


**Structure of**

**Graphite**
- Top: Basal (“graphene”) planes
- Bottom: 3-D view

**Diamond**
- Top: Elemental cell
- Bottom: 3-D view

**Electronic Structure of C-Atom in the ground state:** $1s^2 \ 2s^2 \ 2p^2$

The paired $2s^2$ electrons cannot form bond with a neighbor.

To form chemical bonds, the $2s$ electron is promoted to $2p$ so that C form 4 covalent bonds (see right).

The energy needed for this promotion to $sp^3$ is compensated for by the formation of 4 covalent bonds. However, the remaining 2s electron has to be somehow involved as e.g. in CH$_4$. This is achieved by the hybridization (see below):.

- **$sp^3$ hybridized orbitals in diamond**

If only two 2p hybridize with the remaining 2s orbitals forming $sp^2$
hybrid with three bonds within one plane, one 2p orbital will be left perpendicular to the plane of the three $sp^2$ hybrid thus forming a double bond together with one of the $sp^2$ bonds.

- **$sp^2$ hybrid in graphite**
  - left: top view, right: 3-D view
Graphite, Diamond and Diamond-Like Carbon ("DLC")

Thermodynamical stability and $sp^2 \rightarrow sp^3$ promotion energy


Diamond is with +1.9 kJ/mol metastable with respect to graphite however, the $sp^2 \rightarrow sp^3$ transition requires a high activation energy of about 700 kJ/mol $\approx H_{vap}$. (Graphite) $\rightarrow G \rightarrow D$ transition difficult

Methods of $G \rightarrow D$ transition:
- High P & T with shear loading or in liquid state at $> 60$ kbar
- High P & T & Metals solvent catalyst in the marked region

Also the $D \rightarrow G$ transition requires activation or evaporation:
- $T \geq 900$ K in air
- $T \geq 2400$ K in vacuum

The P – T phase diagram of carbon

F. B. Bundy et al., Carbon 34 (1996) 141
C-H-O Phase Diagram for the Deposition of Diamond and Non-Diamond Carbon in Glow Discharge Plasmas


The diamond is deposited within the region close to the solubility limit of carbon in the H & O containing plasmas. Because the solubility depends on the plasma density (see Veprek loc. cit.), there is a certain variation of the “solubility limit” in different publications. Diamond coatings are grown either in microwave glow discharge or in thermal plasmas at about 800 °C (see Robertson loc. cit.) or by hot wire technique from CH₄ + H₂ mixture.

Single-phase nanocrystalline diamond films are grown under special conditions, the precursors forming the films are believed to be C₂


→ The diamond-like carbon(s) is grown in the non-diamond carbon growth region under energetic ion bombardment.
→ Without ion bombardment polymeric CₙHₘ Films (“Plasma Polymers”) will be deposited from the CₙHₘ containing plasmas.
Meaning & Deposition of Diamond Like Carbon (DLC)

DLC has a broad meaning, but in all cases it contains a three-dimensional network of C-C sp² bonds and a certain fraction of “diamond-like” sp³ four-fold coordinated C-atoms.

Because DLC is deposited either from CHₙ + H₂ mixture or without hydrogen (e.g. by vacuum arc evaporation), a large variety of these materials depicted in figure left exists (from Robertson, loc. cit.)

Promotion of sp² carbon to sp³

Energetic ion bombardment during the deposition causes displacement of the carbon atoms in the growing film, which are within the projected range (“subplantation”) from their positions. Because the displacement energy of sp² carbon of about 20 eV is smaller than that of the sp³ of about 60-80 eV, the ion bombardment “converts” sp² to sp³, as illustrated in Fig. right. Line – calculated, points experiment (see Robertson and references therein.))

→ Glassy C & sputtered a-C:(H) small sp³ fraction but 3-D cross-linking of sp² bonded C atoms.
→ ta-C (tetrahedral carbon) has a high fraction of sp³ bonded C; it can be hydrogen free when deposited by vacuum arc evaporation or contain hydrogen when deposited from hydrocarbons. In the latter case part of the sp³ C-bonds are saturated with H.
→ Hydrogen-free ta-C reaches hardness of 80 GPa, but is relatively brittle.
→ a-C:H has hardness 10-20 GPa and, high elasticity and low friction. For “ta-C:H” the hardness increases up to 50 GPa.

The large variety of the properties of “DLC” carbon finds a large variety of its applications (see Robertson, Gruen and Erdemir et al.)
Coatings for components.

Valve train components:
- Tappets
- Needles, orifices, control plungers, pump plungers

Requirements:
- Pressures > 2000 bar
- Tight closing of the fuel valve
- High speed/high impact closing of the fuel valve
- High speed open close for multiple injections
- Lubrication by Diesel only
- Lifetime Multimillion Injections
- Low cost

Market penetration: Almost 100%
Coatings for components.

**Engine components:**
- Piston pins: DLC.
- Piston rings: CrN
Cost reduction aspects.

Estimated: 450 Mio Components are yearly coated in Hauzer Machines
**DLC² Coating in High Performance Racing Engines**

**Demanding Engine Applications for Racing Cars**

1. **Mechanical lifter (M2 steel, 63-64 HRC)**
   - Contact partner: tool steel camshaft with case hardened lobes
   - No material transfer to the foot
   - Low friction and high wear resistance

2. **Intake valve (Ti alloy)**
   - Contact partner: AMCO45, Ni-Al Bronze alloy
   - No material transfer to the seat
   - Low friction on the stem

3. **Wrist pin (PM-HSS)**
   - Contact partner: tool steel
   - No material transfer
   - Very low friction and low wear

---

Camshaft with CROMV1c²®

Control lever for cylinder head of a racing car with Fi-V1c®

V8 engine, up to 9'000 RPMs, 750 HP
Engine – Surface Treatments: technologies at Sulzer Metaplas

- Nitriding
- Nitriding + Oxidation
- PVD

Injecteds
Camshafts
Tappets
Valve springs
Valves
Valve seats
Piston rings
Pistons
Bearings
Crankshafts

Gear wheels
Rocker arms
Guide pins
Rail guides
Sprockets
Injection pump covers

3ds max®

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Properties & Applications of DLC & DLC-based nanocomposites

- Low coefficient of friction 0.01 - 0.1
- High hardness 16 - > 40 GPa
- Chemically inert
- Biocompatible

Dependence of the Coefficient of Friction on Sliding Speed

Surface asperities “locked-in”

Increasing oil viscosity

Steel against steel oil lubricated

DLC

DLC

0
Sliding Speed
Many different coatings
Nitrides, Carbonitrides, Carbides, Borides …
DLC, Polycrystalline CVD Diamond

…

Here we concentrate on Nitride-based Nanocomposites

1. Understanding Origin of their hardness
2. Industrial Applications
3. Often in Combination with Conventional Coatings
Mechanisms of Hardness Enhancement
“The Strongest Size” vs. Strong Interface

“the Strongest Size”

Hall-Petch Strengthening:
Decrease of dislocation activity with decreasing crystallite size
And other mechanisms of plasticity: slip, twinning, shear …

Below about 10-15 nm strong increase of the material fraction in Grain Boundaries
→ Softening due to G. B. Shear
→ Limited H-Enhancement

Can we reduce the G.B. Shear and move to smaller crystallite size?

Yes we can!
by forming low-energy interfaces (stacking faults, twinning) in Mg-alloys, nt-c-BN (H=108 GPa, nt-Diamond (H=200 GPa!)
or
strengthened interfacial layers in nc-TmN/\text{Si}_3\text{N}_4 Nanocomposites (Tm = Ti, V, TiAlN, CrAlN)

Randomly oriented 3-4 nm size TiN polycrystals are stronger than a single crystal because of higher electronegativity of Si as compared with Ti.

The 1 monolayer thick interfacial Si$_3$N$_4$ strengthened by valence charge transfer.
Superhard Nanocomposite with Strengthened Interface


→ Randomly oriented 3-4 nm size polycrystal is stronger than a single crystal
→ the 1 monolayer thick interfacial Si$_3$N$_4$ strengthened by valence charge transfer

because of higher electronegativity of Si as compared with Ti

Valence Charge Density Difference (DFT)
→ larger VCD on SiN$_x$ than in TiN

81(2010)245418
85(2012)195403
Quasi-ternary nc-TiN/Si$_3$N$_4$/TiSi$_2$ Nanocomposites Prepared by Plasma CVD

Tech. Univ. Munich

6.1 µm thick nc-TiN/a-Si$_3$N$_4$/TiSi$_2$, load 1 N
Indent. depth ≈ 2 µm → >15% elastic in the coating

Li Shizhi et al. 1992

Evaporate Pt strip & focused Ga ion beam etching
S. Veprek in C.C. Koch et al. Structural Nanocrystalline Materials, Cambridge University Press, 2007, Fig. 4.42
Quasi-ternary nc-TiN/Si$_3$N$_4$/TiSi$_2$ Nanocomposites
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Tech. Univ. Munich

† measured
○ non-linear Finite Element Modeling
M.G.J. Veprek-Heijman & S. Veprek, 2014 Submitted

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6.1 µm thick nc-TiN/a-Si$_3$N$_4$/TiSi$_2$, load 1 N
Indent. depth ≈ 2 µm → >15% elastic in the coating

Correct hardness of coatings by Li Shizhi et al. 1992
calculated by non-linear FEM

Evaporate Pt strip & focused Ga ion beam etching
S. Veprek in C.C. Koch et al. Structural Nanocrystalline Materials, Cambridge University Press, 2007, Fig. 4.42
1. The quasi-ternary nc-TiN/a-Si$_3$N$_4$/TiSi$_2$ are unstable in long-terms because of the metastable TiSi$_2$
2. The quasi-binary nc-TiN/Si$_3$N$_4$ are stable for years (measured up to 5 Y)
3. The quasi-binary are more sensitive to oxygen impurities, but H $\approx$ 65-70 GPa has been reported when [O] $\approx$ 100 ppm.

SEM Micrograph of an indentation into about 8 µm thick nc-TiN/Si$_3$N$_4$ coatings with a load of 110 mN


Why such High sensitivity?
100 ppm Bi makes Cu brittle

Impurities $\rightarrow$ embrittlement
Questions:
Why no other researchers reproduced these results for nc-TiN/Si$_3$N$_4$ and other nc-TmN/XY?

Impurities & inappropriate nc-Tm/XY systems

Properties

Why such High sensitivity? 100 ppm Bi makes Cu brittle

Impurities $\rightarrow$ embrittlement
High Thermal Stability 1100 - 1200°C because of the strong interface

nc-TiN/a-Si$_3$N$_4$


nc-(TiAl)N/a-Si$_3$N$_4$

Absence of (TiAl)N decomposition ≤ 1200°C

Stability to ≥ 65 % of $T_{\text{decomp}}$ → stabilization of the SiN$_x$ interface

More stable than TiAlN (and WC-Co) because AlN cannot segregate to the G. B.
Strong Dense Interface (not “protecting surface oxide layer”) → High Thermal Stability and Oxidation & Corrosion Resistance

nc-TiN/a-Si$_3$N$_4$ Coating with 10.5 at.% Si after Oxidation in Air at 900 °C/1 hr → no surface protecting oxide layer

2. Limits to their Preparation

a) Long-term stability

b) Inappropriate deposition condition

c) Impurities

d) The TmN/XY system not spinodal (too small de-mixing energy)

e) Instability of the XY interfacial layer

Homepage: stan.veprek.net
2. Limits to their Preparation

a) Long-term stability

b) Inappropriate deposition condition (too low $T_{dep.}$ & $P(N_2)$

c) Impurities

d) The TmN/XY system not spinodal (too small de-mixing energy)

e) Instability of the XY interfacial layer

Homepage: stan.veprek.net
2. Limits to their Preparation

a) Long-term stability (see above)

b) Inappropriate deposition condition

c) Impurities

d) The TmN/XY system not spinodal (too small de-mixing energy)

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Homepage: stan.veprek.net
Limits to the preparation of ultrahard nanocomposites:

2a) the nc-TiN/Si$_3$N$_4$ system


at 0.5 at.% $\rightarrow$ 20 O-related defects per TiN nanocrystal $\rightarrow$ H determined by defects

0.01 at.% 1 O-related defect per 2-3 TiN nanocrystal $\rightarrow$ approaching defect-free system

Maximum achievable hardness vs. O-impurities

Published papers of other groups: [O] 0.5 – ≥ 2 at.%

SHM company

H-enhancement due to smaller crystallite size
2. Limits to their Preparation

a) Long-term stability

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Homepage: stan.veprek.net
2. Limits to their Preparation

a) Long-term stability

b) Inappropriate deposition condition

c) Impurities

d) The TmN/XY system not spinodal (too small de-mixing energy)

e) Instability of the XY interfacial layer
   (first-principles QMD calculations)

Homepage: stan.veprek.net
Selected Examples of Industrial Applications of Hard and Superhard Nanocomposite Coatings on Tools

Importance of the Impurities Control

→ Impurities are the main obstacle

→ majority of the companies not “superhard nanocomposites” but “the strongest size”
Improvement of deposition conditions in industrial coating unit $\pi^{80}$

higher $T_{dep}$ & lower O-impurities $\Rightarrow$ tool life time improvement by > 100 %

S. Veprek, M. Veprek-Heijman (Tech. University Munich), X. Zeng (SIMTech, Singapore), M. Píška (Tech. University Brno, CZ), A. Bergmaier (Univ. Bundeswehr Munich)

lower O-impurities!

Steel DIN C45

\[ C \quad Mn \quad Si \quad P \quad S \quad Cr \quad Ni \quad Fe \]
\[ 0.42-0.5 \quad 0.5-0.8 \quad 0.17-0.37 \quad 0.004 \quad 0.004 \quad 0.25 \quad 0.3 \quad \text{balance} \]

$V_C = 130 \text{ m/min}$

$\begin{align*}
&f = 0.18 \text{ mm/revolution} \\
&a_F = 1.5 \text{ mm} \\
\end{align*}$

Improved deposition 1
4 Inserts

Improved deposition 2
4 Inserts

2.2 x

\[ 0.2-0.3 \text{ at.\% Oxygen} \]

\[ \leq 0.1 \text{ at.\% Oxygen} \]

$\text{cutting speed on depth of cut}$
Detrimental Effect of Oxygen Impurities


Good News

Surface contamination

0.07 at.% = 700 ppm

We need an improvement only by a factor of 3-4 to reach ≤ 250 ppm in the industrial coating units!

The great challenge:

Presently ≤ 1000 ppm impurities in every day deposition in “ORM” of SHM and in Pi80 & Pi300 of PLATIT

Plastic Hardness [GPa]

Oxygen Content [at%]

SHM & TUM
Industrial Coating System “ORM”

The columnar morphology typical of PVD coatings decreases and vanishes for nanocomposites.
Variety of the “Architecture” of Coatings on Tools

- Monoblock with adhesion layer
- Multilayers
- Gradient layer

Continuous cutting
Interrupted (milling)
Hard & Dry machining

Nanolayered structure
Nanocomposite
Triple Coatings

Costs of Machining

Decreasing Total Costs by Increasing Cutting Speed and Tool Life-Time

→ and Dry Machining

Costs (r.u.)

Tools
Maintenance
Capital
Total

Cutting Speed (r.u.)
Productivity

Tools:
- Increase speed
- Increase lifetime
- Reduce TOTAL Costs

Need for low wear at:
- high cutting speed
- high temperature

high temperature stability and oxidation resistance
3. Selected Examples of Industrial Applications of Hard and Superhard Nanocomposite Coatings on Tools

b) Selected Examples

→ What are the advantages of the superhard nanocomposites
Advantages of Superhard Nanocomposites:
- Higher Hardness
- Higher oxidation & corrosion resistance
- Lower thermal conductivity $\rightarrow$ lower heat flow into the cutting edge
- Higher cutting speed & feed $\rightarrow$ Higher Productivity
- Longer Life Time of Expensive Tools
- Dry Cutting – economy, ecology
- Flexibility in the design of “triple Coatings”

Presently Available Superhard Nanocomposite Coatings for Industrial Applications:

$\rightarrow$ nc-$(Ti_{1-x}Al_x)N/a-Si_3N_4$ - ("TiAlSiN” or ”AlTiSiN”)

$\rightarrow$ nc-$(Cr_{1-x}Al_x)N/a-Si_3N_4$ ("CrAlSiN”)

TiCrN/Ni not superhard ($H \approx 15 – 20$ GPa) but ductile $\rightarrow$ forming
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$\rightarrow$ nc-$\text{(Cr}_{1-x}\text{Al}_{x})\text{N/a-Si}_{3}\text{N}_{4}$ (“CrAlSiN”)

TiCrN/Ni not superhard (H $\approx$ 15 – 20 GPa) but ductile $\rightarrow$ forming
Oxidation Resistance of Commercial (TiAl)N Coatings and of the Nanocomposites nc-(TiAl)N/a-Si₃N₄ with dense interface

900°C in air, 60 min

(TiAl)N
Manufacturer A

(TiAl)N
Manufacturer B

nc-(AlTi)N/a-Si₃N₄

Oxidation Resistance of nc-(AlTi)N/a-Si₃N₄ about 4x Higher  ➔ 4x Better Cutting Performance
Drilling

SHM, s.r.o., Průmyslová 3, CZ-787 01 Šumperk
PLATIT A.G., Grenchen, Switzerland

Workpiece: X155 CrVMo 12-1 - DIN 1.2379 Cold working steel

Tools: HM drills - d=5mm - ap=15 mm - vc=70 m/min - f=0.16 mm/rev - emulsion 7%

State-of-the-art (AlTi)N

4x nanocomposites

Tool life (holes when VB=0.2mm)
Advantages of Superhard Nanocomposites:
- Higher Hardness
- Higher oxidation & corrosion resistance
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- Higher cutting speed & feed $\rightarrow$ Higher Productivity
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$\text{TiCrN/Ni}$ not superhard ($H \approx 15 – 20$ GPa) but ductile $\rightarrow$ forming
Low heat conductivity of the coatings due to high phonon scattering ➔ lower heat flow into the cutting edge of the tool

$\text{AlCrN/\text{Si}_3\text{N}_4 \ (nACo)}$ has a lower thermal conductivity than $(\text{AlCrN})$

From [www.platit.com](http://www.platit.com)

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**Thermal conductivity of AlTiSiN ≈ 0.15 of AlTiN**


END MILLS HSS
Lifetime of conventional coatings decreases with increasing cutting speed whereas that of the nanocomposites increases

Thermal conductivity of nACo << TiAlCN & AlTiN due to large phonon scattering on Grain Boundaries

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Milling distance $L_T$ [m]

- nACo G: 2.8 um
- nARCo G: 3.2 um
- nARCo ML: 2.8 um
- TiAlCN: 2.4 um
- AlTiN: 2-3 um

Cutting speed $v_c$ [m/min]

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T. Cselle PLATIT AG
Advantages of Superhard Nanocomposites:
- Higher Hardness
- Higher oxidation & corrosion resistance
- Lower thermal conductivity → lower heat flow into the cutting edge
- Higher cutting speed & feed → Higher Productivity
- Longer Life Time of Expensive Tools
- Dry Cutting – economy, ecology
- Flexibility in the design of “triple Coatings”

Presently Available Superhard Nanocomposite Coatings for Industrial Applications:

→ nc-(Ti$_{1-x}$Al$_x$)N/a-Si$_3$N$_4$ - (“TiAlSiN” or ”AlTiSiN”)
→ nc-(Cr$_{1-x}$Al$_x$)N/a-Si$_3$N$_4$ (“CrAlSiN”)

TiCrN/Ni not superhard (H ≈ 15 – 20 GPa) but ductile → forming
Hard Dry Milling

T. Cselle, PLATIT A.G. (CH)
Hard Milling of 57 HRC Steel

Ball nose, cemented carbide end mills, d=10 mm, External Minimum Jet Lubrication
18 500 RPM, fz=0.18 mm, ap=0.25 mm, ae=0.6 mm,

2nd Generation: Improved Design of Coatings + higher Si-content

(TiAl)N/Si₃N₄
1st Generation
Fatigue of "WC/Co" Substrate

T. Cselle & M. Morstein, PLATIT AG

Coatings

nACo-MLH-N
nACo-MLH
AlTiN 1
AlTiN 2
nACo-MLH ii
nACo-MLH i
Hard Milling of 57 HRC Steel

Ball nose, cemented carbide end mills, d=10 mm, External Minimum Jet Lubrication
18 500 RPM, fz=0.18 mm, ap=0.25 mm, ae=0.6 mm,

2nd Generation: Improved Design of Coatings + higher Si-content

First TripleCoating: nACo

<table>
<thead>
<tr>
<th>Coating</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>nACo</td>
<td>~0.6μm</td>
</tr>
<tr>
<td>AlTiN</td>
<td>~1.8μm</td>
</tr>
<tr>
<td>Ti-TiN adhesion layer</td>
<td>~300 nm</td>
</tr>
</tbody>
</table>

1st Generation

Fatigue of "WC/Co" Substrate

2nd Generation:

Improved Design of Coatings + higher Si

(TiAl)N/Si₃N₄

Hitachi Nanocomposites

Coatings

TiAlN

nACo-MLH-N

nACo-MLH

AlTiN 1

AlTiN 2

nACo-MLH ii

nACo-MLH i

ol Life-Time [m]

ap-axial -, ae- radial depth of cut
Deposition of Triple Coatings in $\pi^{313}$Coating Unit

Significant advantage of the rotating cylindrical cathodes enables to deposit either TiN or CrN adhesion layer & compound layers with one set of targets:
→ High adhesion of > 150 to 200 N
→ Perfect mixing of different metals

1st step: 300 nm adhesion graded layer of Ti → TiN or Cr → CrN

2nd step: Core layer AlTiN

3rd step: Top layer nATCRO®
Rotating Cathode

Advantages:
1. Longer Life-Time
2. Strong reduction of droplets ("macroparticles"")
3. "Virtual Shutter®"

Track of the cathodic spot
Wall of the chamber
The $\pi$-Advantages - Lower Target Costs

Ti-Target after 467 batches
Pre-Cleaning

- Target cleaning and deposition of large particles against wall
- Magnetic fields turned by 180°

Deposition

- Magnetic fields are turned back after cleaning at 0° for deposition
- Substrates
- Rotary table

ARC is burning to the back; cathode is cleaned
ARC is burning to the substrates; cathode is depositing
Virtual Shutter ⇔ Deposition
The optimum period is adjusted by the rotation speed & deposition rate

Example from CRC ARC
Nano-Layered Nanocomposite (AlTi)N/Si$_3$N$_4$ Coatings
Increase of Hardness & Toughness
Multi-Layers $\rightarrow$ Higher Fracture Toughness because the cracks are deflected and cannot easily propagate through the layer

A. Matthews et al., Tribology Lett. 11 (2001) 103
<table>
<thead>
<tr>
<th>coating</th>
<th>Ra (µm)</th>
<th>Old</th>
<th>New</th>
</tr>
</thead>
<tbody>
<tr>
<td>MARWIN SI</td>
<td>≥ 0.30</td>
<td>≥ 0.30</td>
<td>≤ 0.06</td>
</tr>
<tr>
<td>MARWIN MT</td>
<td>≥ 0.35</td>
<td>≥ 0.35</td>
<td>≤ 0.06</td>
</tr>
</tbody>
</table>

Surface Quality

- TiN
- TiAlSiN
- Old
- CRC & LARC
Maintenance of Railroads for Fast Trains ≤ 320 km/hr

Shinkansen Japan since 1964

TGV France since 1981

ICE Germany since 1993

Required surface roughness of the rails for given speed

≤ 160 km/h - 0.5 mm
160 – 280 km/h – 0.3 mm
> 280 km/h – 0.2 mm
Required surface roughness of the rails for given speed

- $\leq 160$ km/h - 0.5 mm
- 160 – 280 km/h – 0.3 mm
- $> 280$ km/h – 0.2 mm

Milling tool

$D = 600$ mm, $z = 22$ teeths, $v_C = 220 - 280$ m/min, $n = 120 - 150$ rev./min, $f = 700$ m/h, $a_P = 1.5$ mm

Steel R350 HT

$H = 0.9 - 1.2$ GPa $\rightarrow$ 1.5 GPa (cold work hardening)  
(27 – 46 HRC)

Solution: TripleCoatings

Large-scale tests in large European countries
Life Time increase by 30 % as compared with the competitor
$\rightarrow$ “life-time” $> 2$ km!
Advantages of Superhard Nanocomposites:

- Higher Hardness
- Higher oxidation & corrosion resistance
- Lower thermal conductivity $\Rightarrow$ lower heat flow into the cutting edge
- Higher cutting speed & feed $\Rightarrow$ Higher Productivity
- Longer Life Time of Expensive Tools
- Dry Cutting – economy, ecology
- Flexibility in the design of “triple Coatings”

Presently Available Superhard Nanocomposite Coatings for Industrial Applications:

$\Rightarrow$ nc-$\left(\text{Ti}_{1-x}\text{Al}_x\right)$N/a-$\text{Si}_3\text{N}_4$ - (“TiAlSiN” or ”AlTiSiN”) 

$\Rightarrow$ nc-$\left(\text{Cr}_{1-x}\text{Al}_x\right)$N/a-$\text{Si}_3\text{N}_4$ (“CrAlSiN”)

TiCrN/Ni not superhard (H $\approx$ 15 – 20 GPa) but ductile $\Rightarrow$ forming
Drill test in cast iron GGG40
© UNIMERCO DK

Performance improvement at Higher Speed & Feed Rate

Tools: ø7.1-12mm SC step drills - Cooling: 70 bar internal 5% emulsion
Test material: GGG40 - Vc: 140-200 m/min - Vf: 1475 - 2304 mm/min
Source: Sauer Danfoss Steerings, DK

Increase in Productivity with AlTiSiN-Nanocomposites 56 %!
Dry Tapping of HSS

The nc-(AlTi)N/a-Si$_3$N$_4$ Nanocomposites are superior particularly at high cutting speed

T. Cselle
PLATIT
Advantages of Superhard Nanocomposites:
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TiCrN/Ni not superhard ($H \approx 15 – 20$ GPa) but ductile $\rightarrow$ forming
nc-(AlCr)N/Si$_3$N$_4$ = “nACRo®“

- Tool life: No. of produced gears
  - 1: new coated
  - 2: reground
  - 3: reground + recoated

- Lifetime 5x
- Too large scatter

- Coating options:
  - TiCN-TiN
  - AlTiN + TiN cover
  - AlCrN + TiN cover

- nACRo®
Lifetime of Solid Carbide Saw Coated with different Coatings
(Precision Metal Cutting)

Tool Lifetime: number of sawed parts with tolerance of ± 0.2 mm

- AITiN
- nACo®
- nACRn®

Solid Carbide saw blades Diam. 125 mm, Thick. 3.6 mm, z = 100, sintered workpiece material Co1
N = 300 RPM, vf = 800 mm/min, ap = 35 mm, colant: emulsion 7%
Source: Prétat, Selzach & PLATIT AG, CH

T.Cselle PLATIT AG (CH)
Comparison of the lifetime of a tool for stamping of buckles for car safety belts coated with different coatings

Brano a.s. & Liss Roznov, CZ

4x
Drilling the wings of the Airbus 380, Broughton, North Wales, UK

Material: Al-Alloy & graphite fibre reinforced Carbon - SIMULTANEOUSLY

1. 2x longer lifetime of the (less expensive) nanocomposite coatings
2. 5 to 6-times recoat possible → much longer life time of the tool (≥ 250 €)
3. Price per drilled hole reduced 5 to 6x

Nanocomposite C7 coated by Unimerco, UK

Tools: solid carbide drills - d=10-12 mm
Milling of the Ni-based superalloy Inconel 718 of a jet turbine shaft using carbide inserts coated with dedicated coating in comparison with the nanocomposites

Machining of Ni-based superalloys: Strain hardening, high cutting energy, low T-conductivity

(Minimaster MM12, D = 12 mm, vc = 21-30 m/min, fz = 0.05 mm, radial depth of cut ae = 3 mm). Source: MACHERENA & Volvo Aero Norge AS.
Injection Moulding of Aluminum Alloys for Automotive Industry

after the fabrication of 15 000 parts with different surface treatment. The length and diameter of several similar tools which were tested was 180-200 mm and 15-25 mm, respectively.

Conventionally treated

2 to 3 µm thick CrAlN/SiN$_x$ nanocomposite coatings
Advantages of Superhard Nanocomposites:
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- Higher oxidation & corrosion resistance
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TiCrN/Ni not superhard (H $\approx$ 15 – 20 GPa) but ductile $\rightarrow$ forming
Thick Coatings nc-(TiCr)N/Ni on Forming Tools
Hardness ≈ 15-18 GPa; Dep. Rate ≈ 13-16 µm/hr

Deep-drawing of a steel profile

5-6 tools needed

<table>
<thead>
<tr>
<th>production time [min]</th>
<th>drawing</th>
<th>service</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>750</td>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

no measurable wear of the tool

- steel 1.0028
- profile No.47 05 910
- drift pin = 27,5 µm
- die = 62,8 µm
- speed = 8,6 → 13,7m/min
- 1065 pcs x 8 m = 15 tons
Folding of Printed Packaging Cartoon with Coated Segments

High chemical corrosion resistance

![Diagram showing tool life comparison with coated segments](image)

- uncoated: 100
- TiN: 145
- TiCN-MP: 193.4
- nACo®: 342

(TiAl)N-Si3N4
Can a small company use this high tech?
YES it can!

Cutting performance of indexable inserts coated with the state-of-the-art (Ti$_{1-x}$Al$_x$)N coatings and with the Nanocomposites

3D area clearance milling of hard steel 1.2311, cutting speed 190 m/min, feed 0.9, ap = 1, emulsion cooling (M.T.M. Ltd. Castelfidardo, Italy, EU Project RESTOOL)

Also a small company can optimize its machining performance and increase the productivity but it needs access to the know-how
Sharp cutting edge of the tool?
Sharp cutting edge is NOT the best choice because the Coatings there Peel-off

Lifetime of Drills vs. rounding of the cutting edge
Effect of Corner Edge Preparation on the Performance of Drills

Material: cold working steel X155CrVMo12-1–HRC – blind holes;
Drills: Cemented Carbide – nACo coatings d = 5 mm, \( v_c = 75 \text{ m/min} \), \( f_z = 0.15 \text{ mm/z} \), \( a_p = 15 \text{ mm} \), cooling air (no emulsion!)

New tools adapted to new coatings
Many further applications
The superhard nanocomposite coatings
are not the “future nanotechnology”,
they are present reality
But much further improvement needed

For example $[O] < 500$ ppm to coat HSS tools because it softens above $530 \, ^\circ C$
Conclusions & Outlook

1. → Hardness of $\geq 100$ GPa is possible but requires impurities below 100 ppm.

   **Challenge for the Academia**

   → Long-term stable hardness of about 70 GPa has been demonstrated in quasi-binary nc-TiN/Si$_3$N$_4$ nanocomposites with [O] $\approx 100$ ppm.

2. Limits for achieving high hardness:
   - Impurities → Impossible to form nc-TiN/Si$_3$N$_4$-like nanocomposites
     Unfortunately majority of reported coatings have 0.5 to $\geq 2$ % of oxygen;
     These are not „superhard nanocomposites“
   - for other limits see Thin Solid Films 522 (2012) 274

3. The hard and superhard nanocomposites are already in industrial applications

4. Further improvement, in particularly higher purity is needed
   challenge for the - Industry: get O-impurities down to 200-300 ppm
   - Academia: get O-impurities to few 10 ppm $\Rightarrow H \approx 80 – 100$ GPa

**Thank you for your attention**

Any questions?: stan@veprek.net

Homepage: stan.veprek.net $\Rightarrow$ Next week