Nanokompositschichten - Konzepte, Synthese und analytische Herausforderungen

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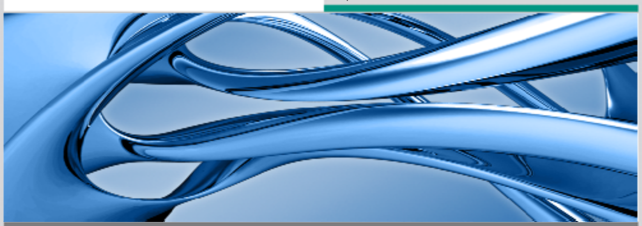


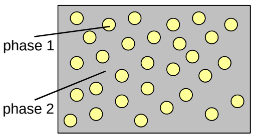
Outline

- indroduction: concepts for nanocomposite coatings
- metastable materials as multifunctional components for nanocomposite coatings
  - nanocrystalline metastable hard coatings: structural und functional design, coating concept thermodynamics, key parameters
  - experimental setup: r.f. magnetron sputtering
  - results and discussions: f.c.c. (Ti,Al)(C,N)
  - summary f.c.c (Ti,Al)(C,N)
- carbon-based nanocomposite coatings
  - experimental setup: r.f. magnetron sputtering
  - results and disscusion: (Ti,Al)(C,N) / a-C
  - summary nanocomposites

Concepts for multifunctional wear-resistant thin film nanocomposites

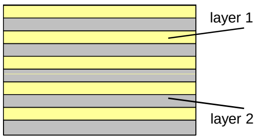
Basic characteristics: multiphase structure, at least one phase has dimensions in the nm-range

multiphase single-layer coatings



phase 1: nanocrystalline
phase 2: nanocrystalline or amorphous
matrix phase + dispersed phase or percolated network

nanoscale multilayer coatings



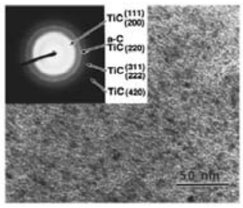
layer 1: single- or multiphase
layer 2: single- or multiphase, but different
multilayers, superlattices, nanostabilisation or nanolaminated composites

Synthesis of materials with new properties by engineering design of their nanoscale microstructure

Nanocomposite coatings with amorphous carbon and nanocrystalline hard phases

Objective: to design wear-resistant and lubricious coatings with tailored hardness and toughness

Example: TiC/a-C coatings



A.A. Voevodin, S.V. Prasad, J.S. Zabinski, J. Appl. Phys. 82 (2) (1997) 855.

Concepts for carbon-based nanocomposite coatings

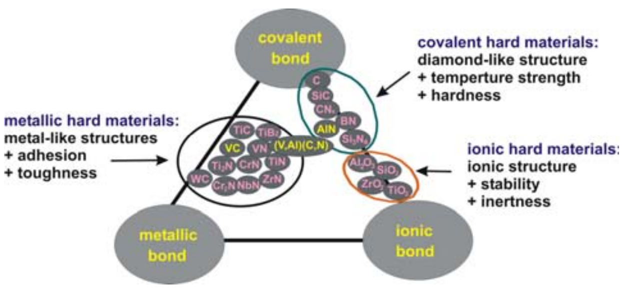
binary carbide phase + a-C: WC/a-C, TiC/a-C
Dimigen, Klages, Benndorf, Grischke, Sjöström, Sundgren, Voevodin, Monteiro, Hogmark, Wiklund, Patscheider, Wänstrand, Park, Pauleau, Gulbinski, Pei, De Hosson et al.

binary non-carbide hard phase + a-C: TiB_2/a-C
Gilmore, Gissler, Mitterer, IMF I,
only a few reports available

metastable hard phase + a-C: (Ti,Al)(N,C)/a-C
(Ti,Cr)(N,C)/a-C
Shieh & Hon [2002/2005, CVD], Zhang [2002], Lackner [2004], IMF I [2005],
emerging new class of material ?

hard phase + lubricious phase + a-C: WS_2/WC/a-C
Voevodin, Zabinski, Cavaleiro et al.

Structural and functional design



Coating concept for multifunctional metastable coatings

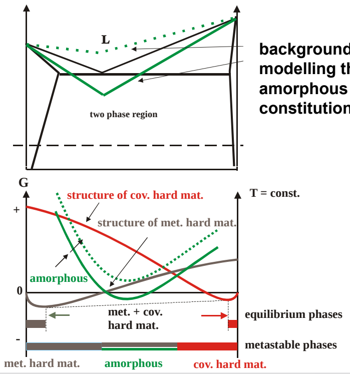
stabilization of covalent hard materials in a metal-like structure ⇒ combination of high + temperature strenght + hardness + adhesion + toughness ⇒ realization: nanocrystalline metastable fcc (V,Al)(C,N)

Thermodynamics of quasibinary sections in hard material systems

phase diagrams for hard material systems with limited, but different solubilities (schematic)

background of modelling the amorphous film constitution

free energies of formation (schematic) for systems with metallic and covalent hard materials



Estimation of free energies of metastable film materials by combining lattice stability with the regular solution model

$$G = \sum_i n_i G_i + G_m \qquad \Delta G = \sum_i n_i \Delta G_i + \Delta G_m$$

lattice stability

metallic hard materials in the structure of covalent or ionic hard materials
(ΔG_i~ +70 kJ/mol)

covalent or ionic hard materials in the structure of metallic hard materials
(ΔG_i ~ +30 kJ/mol)

amorphous film materials
(ΔG_i ~ +20-50 kJ/mol)

free energy of mixing
(regular solution model)

$$\Delta G_m = \Delta H_m - T\Delta S_m^{id} \qquad \left(T\Delta S_m^{exc.} = 0\right)$$

$$\varepsilon x_A x_B \qquad \Delta S_m^{id} = R\,(x_A \ln x_A + x_B \ln x_B)$$

$$x_B = 1 - x_A$$

$$\varepsilon = \left(H_{AB} - \frac{H_{AA} + H_{BB}}{2}\right)$$

ε ~ 160 kJ/mol·d – 30 kJ/mol

The interaction energy ε as a key parameter for the formation of metastable materials

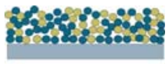
$\varepsilon_{E1E2\text{-}AlN}$ ↓

⇒ ↑ possible composition range for metastable materials

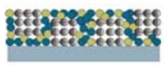
⇒ ↑ enhancement of parameter range of deposition (T_{sub}, E_{ion}, P_{ion}) for metastable materials

⇒ ↓ decreasing of parameter range for the formation of amorphous materials

Qualitative correlation between film constitution and diffusion distance l_D



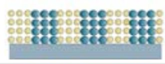
a-VCAlN
l_D = 0.5 - 1 nm



nc-fcc-VC+a-AlNVC
nc-fcc-VC+a-AlN
l_D = 4 - 6 nm

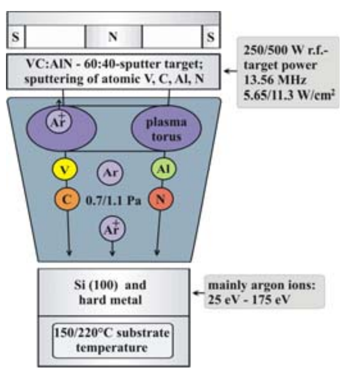
nc-disordered metastable fcc-(V,Al)(C,N)
nc-disordered metastable hex-(Al,V)(N,C)
l_D > 6 nm

nc-ordered metastable fcc-(V,Al)(C,N)
nc-ordered metastable hex-(Al,V)(N,C)
l_D > 10 nm



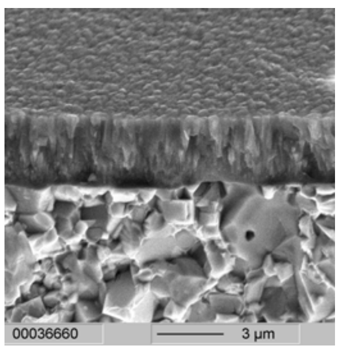
nanocomposites:
nc-fcc-VC + nc-hex-AlN
l_D > 100 nm

r.f. magnetron sputtering

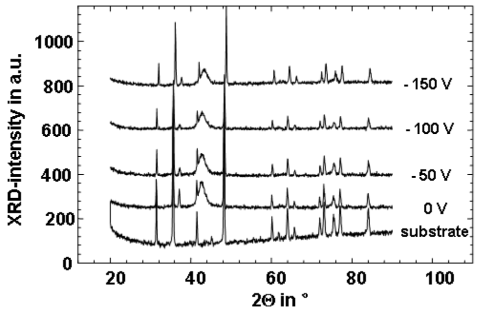


$P_{r.f.,Target}$ = 250 W
p_{Ar} = 1.1 Pa
T_S = 150 °C

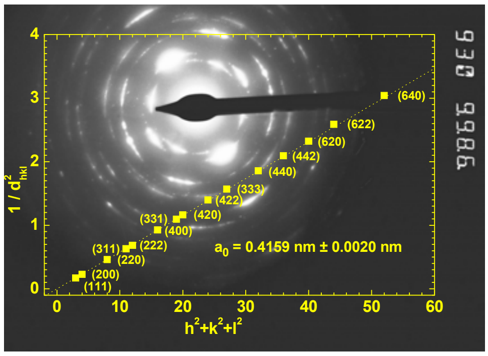
SEM analysis of V-C-Al-N coatings



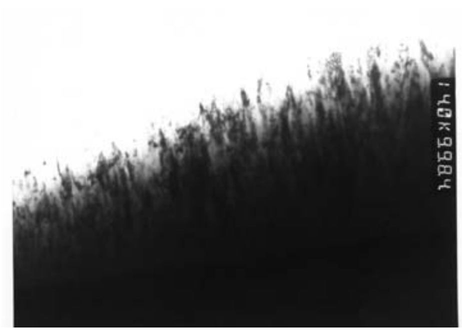
XRD investigations of nanocrystalline metastable f.c.c. (V,Al)(C,N)



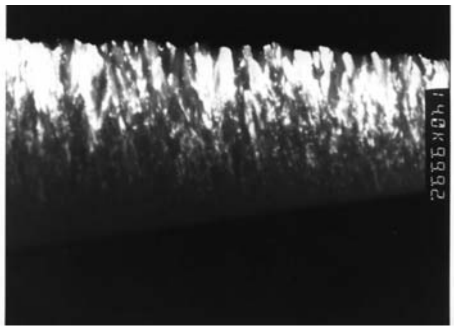
TEM investigations of nanocrystalline metastable f.c.c. (V,Al)(C,N)



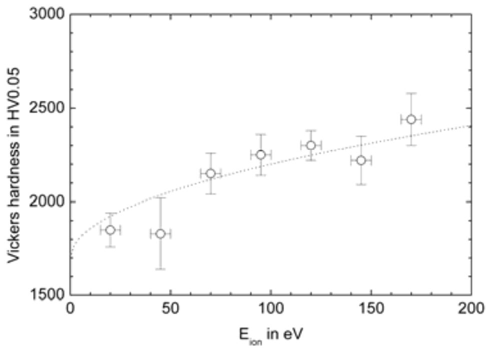
TEM investigations (bright field) of nanocrystalline metastable f.c.c. (V,Al)(C,N)



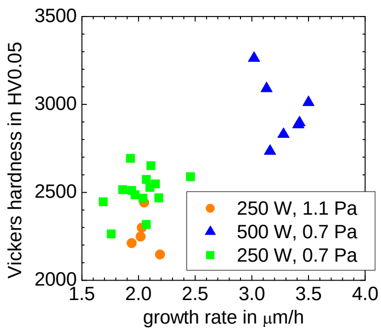
TEM investigations (dark field) of nanocrystalline metastable f.c.c. (V,Al)(C,N)



Vickers hardness of nanocrystalline V-C-Al-N coatings



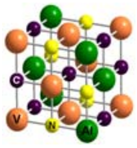
Vickers hardness of nanocrystalline V-C-Al-N coatings



Summary: nanocrystalline, metastable f.c.c (V,Al)(C,N)

thermodynamic modelling

key parameters for the formation of metastable thin films



magnetron sputtering

$P_{r.f.,target}$ = 250 / 500 W
ν = 13.56 MHz
VC : AlN = 60 : 40
p_{Ar} = 0.7 / 1.1 Pa
T_S = 150 / 220°C
E_{Ar+} = 25 – 175 eV
R = 1.69 – 3.5 µm/h

constitution

zone 1 and T
nanocrystalline
metastable
fcc $(V_{0.3},Al_{0.2})(C_{0.3},N_{0.2})$
$d_{crystall}$ = 4 – 10 nm
a_0 = 0.4159 ± 0.0020 nm

mechanical properties

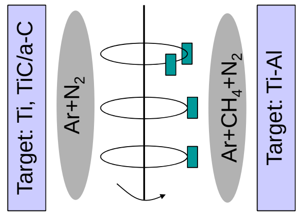
Vickers hardness
1850 – 3260 HV0.05
$E/(1-\nu^2)$
450 – 520 GPa
L_c = 25 – 50 N

Magnetron-sputtering of nanocomposite coatings in the system Ti-Al-N-C

equipment: Hauzer HTC 625 machine,
1 or 2 target-configuration resp.

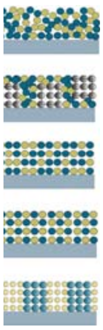
targets: commercial TiAl (Ti:Al 50/50), Ti, and TiC/a-C 30/70,
size: 400 mm x 125 mm

process parameters
Ar flow: 200 sccm
sputtering power: 3 - 6 KW
substrate bias: 80 V
N_2 flow: 0 - 32 sccm
CH_4 flow: 0 – 30 sccm
temperature: 100 - 400°C



scheme of deposition

Metastable nanocrystalline fcc (V,Al)(C,N) hard coatings



a-VCAlN
l_D = 0.5 - 1 nm

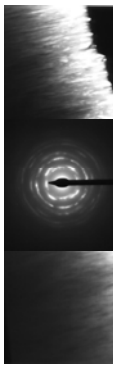
nc-fcc-VC+a-AlNVC
nc-fcc-VC+a-AlN
l_D = 4 - 6 nm

nc-disordered metastable fcc-(V,Al)(C,N)
nc-disordered metastable hex-(Al,V)(N,C)
l_D > 6 nm

nc-ordered metastable fcc-(V,Al)(C,N)
nc-ordered metastable hex-(Al,V)(N,C)
l_D > 10 nm

nanocomposites:
nc-fcc-VC + nc-hex-AlN
l_D > 100 nm

Correlation between film constitution and diffusion length l_D



rf magnetron sputtering
VC/AlN 60:40 target
220°C, -175 V bias

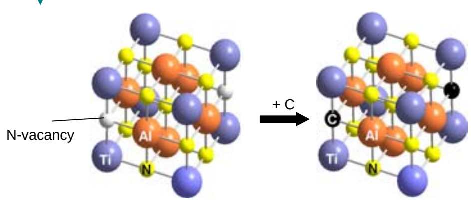
nanocrystalline, fcc
$(V_{0.3}Al_{0.2})(C_{0.3}N_{0.2})$
crystallite size
< 10 nm
a_0 = 0.4102 nm
$a_{0,\,VC}$ = 0.4159 nm

up to 3200 HV0.05
up to 520 GPa
(VC: 2300 HV0.05)
(AlN: 1200 HV0.05)

Growth model of magnetron-sputtered (Ti,Al)(N,C)/a-C nanocomposite coatings

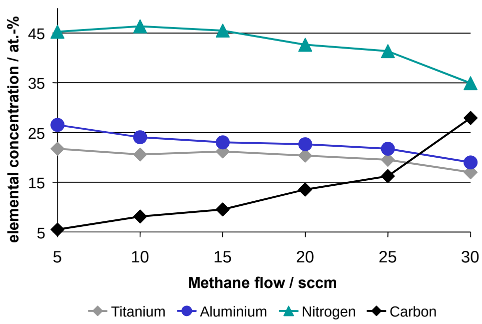
C concentration

five-step growth model of Ti-Al-N-C nanocomposite coatings:
- start from sub-stoichiometric fcc $TiAlN_{1-x}$
- fill in N-vacancies by C atoms
- substitute regularly N atoms by C atoms
- build carbon nano-clusters/agglomerates
- build continuous carbon phase



M.Stueber et al., Thin Solid Films 493 (2005) 104

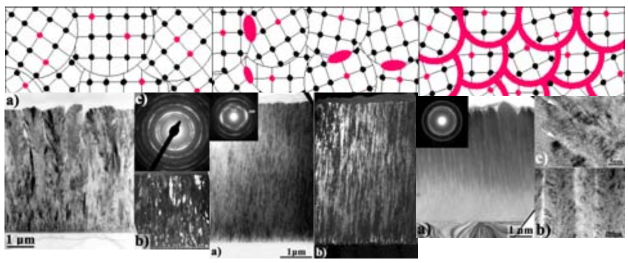
Chemical composition of magnetron-sputtered Ti-Al-N-C-coatings



Characterisation method: electron probe micro analysis (Cameca microbeam system)

Carbon-based nanocomposite coatings – the (Ti,Al)(N,C)/a-C example

reactive d.c. magnetron sputtering, Hauzer HTC 625 machine, TiAl 50/50 targets, 200°C, -60 V bias



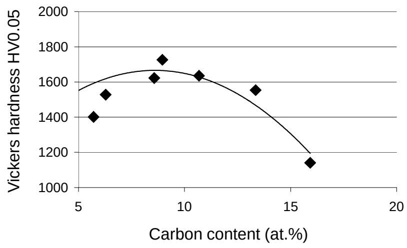
0 < at.-% C < 8
metastable solid solution
single-phase fcc (Ti,Al)(N,C)

8 < at.-% C < 16.5
isolated carbon nanoclusters

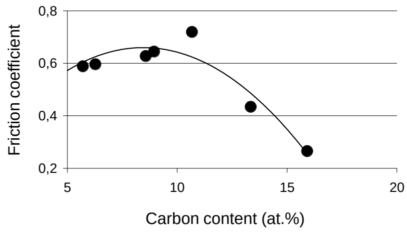
16.5 < at.-% C < 28
a-C grain boundary phase

nanocomposite structures (Ti,Al)(N,C)/a-C

Selected properties of Ti-Al-N-C coatings as a function of carbon content: Vickers hardness



Selected properties of Ti-Al-N-C coatings as a function of carbon content: friction coefficient



Pin-on-disk model testing (CSM Reve-Test)
unlubricated sliding friction against 100Cr6 ball
10 N, 1000 m, 3 cm/s

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Coatings selected for dry cutting tests (milling operation)

Nanostructured carbon composite coating	name	No. of layers	C content of Ti-Al-N-C layer	$T_{sub.}$ (°C)	HV 0.05	Δ (d_1/d_2)	operation: milling of		
							Orvar	Rigor	hex. C
single layer coating (Ti,Al)(N,C)/a-C	A1(A1*)	1	13.5 at.-%	200	2050		X	X	(X)
	A2	1	13.5 at.-%	400	1670				X
multilayer coating (Ti,Al)(N,C)/a-C + TiN	B1(B1*)	50	8.1 at.-%	400	2050	2.2			X
	B2(B2*)	50	8.1 at.-%	400	1840	10	X	X	(X)
	B3	50	13.5 at.-%	400	1880	8.8	X	X	
multilayer coating (Ti,Al)(N,C)/a-C + TiC/a-C	C1	100	13.5 at.-%	100	2070	1	X	X	
	C2	100	13.5 at.-%	100	2440	1			X

Benchmarking with industrial reference coatings (various suppliers)
R1 – TiAlN single layer coating, R2 – TiAlYCrN multilayer coating,
R3 – TiAlN single layer coating, R4 – TiAlN multilayer coating, R5 – TiN single layer coating

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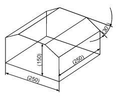
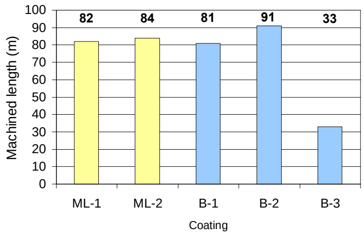
Performance of multilayer coatings with (Ti,Al)(N,C)/a-C nanocomposite layers

wear studies and cutting tests in dry high speed ramp copy milling of A2 cold work steel (1% C & 5.3% Cr)
multilayer coatings ML-1, ML-2: 50 layers of (Ti,Al)(N,C)/a-C + TiN, hardness 2000 HV0.05
coatings B-1, B-2, B-3 are industrial benchmark coatings (both TiAlN- and TiN-based)

micro-grain grade cemented carbide tools



slab, slope 30°



cutting conditions
S: 15000 rpm
F: 9000 mm/min
ae: 0.3 mm, ap: 0.3 mm
compressed air: 6 bar

stop criterium: tool life

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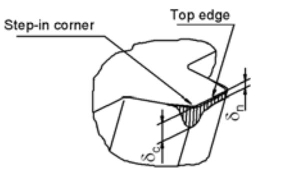
Model wear test for simulating gear cutting operations

simplified cutting-edge duration analysis
(similar to the fly hobbing method)
Bouzakis & Antoniadis,
Annals of the CIRP 37 (1988) 109-112
equipment: Liebherr machine



main wear characteristics on a hobbing tool

single-tooth tools (powdermetallurgical HSS)

THYSSEN TSP 30 tool inserts, tool diameter: 100 mm

experimental conditions for cutting tests
- workpiece made of 16MnCr5 steel (gearbox)
- cutting speed 98.96 m/min
- tangential feed 0.388 mm/min (conditions chosen from hobbing with lubricants)
- criterion for evaluation of tool performance: wear on tool edge > 0.2 mm

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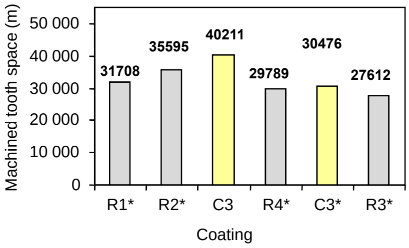
Results of model wear tests in gear cutting of 16MnCr5 steel



R1*, R2* - industrial reference coatings:
TiN single layer, tested in oil lubrication (state-of-the-art)
R3*, R4* - industrial reference coatings:
Ti-Al-N based multilayer, tested in dry conditions
C3, C3* - multilayer coatings (Ti,Al)(N,C)/a-C + TiC/a-C, tested in dry conditions, no built-up edges

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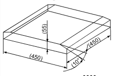
Ramp copy milling of graphite POCO EDM-200 (lab-scale)

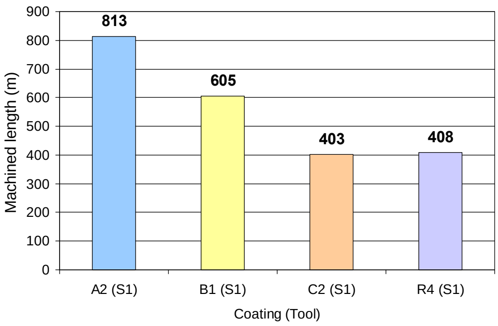
slab, slope 10°



ramp copy milling

<u>cutting conditions</u>:
S: 11000 rpm
F: 3800 mm/min
ae: 0.2 mm
ap: 1.0 mm

<u>stop criterium</u>:
tool life



Summary: (Ti,Al)(C,N)/a-C nanocomposite coatings

- **significant improvement of thin film properties (hardness, elastic moduli, intrinsic stress) by**
  - **appropriate material selection and adjusting of kinetic and energetic conditions of PVD film growth**
  - **design of specific nanoscale multilayer architectures**
  - **superfine structural ordering at the nanoscale (grain boundaries + interfaces)**
- **nanocomposite formation in carbon-based systems – elastic coupling of nanograins and layers through amorphous carbon at grain boundaries, column boundaries and at interfaces**