mechanical properties of thin films & hard coating materials

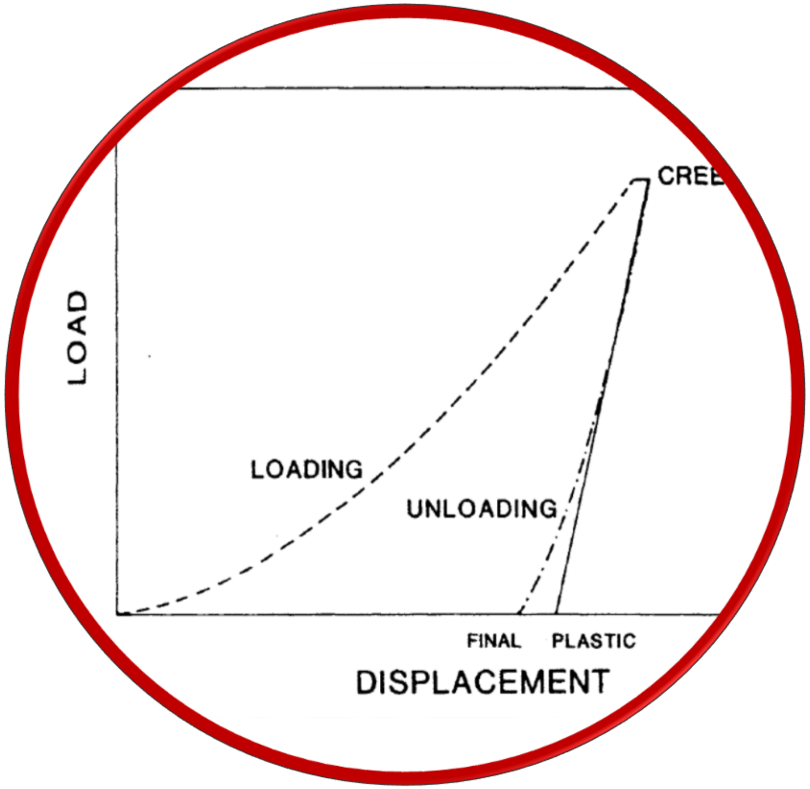


Table of contents I

- **Adhesion of thin films**
  - Interfacial fracture mechanics
  - Strategies to increase adhesion
  - Techniques to measure adhesion

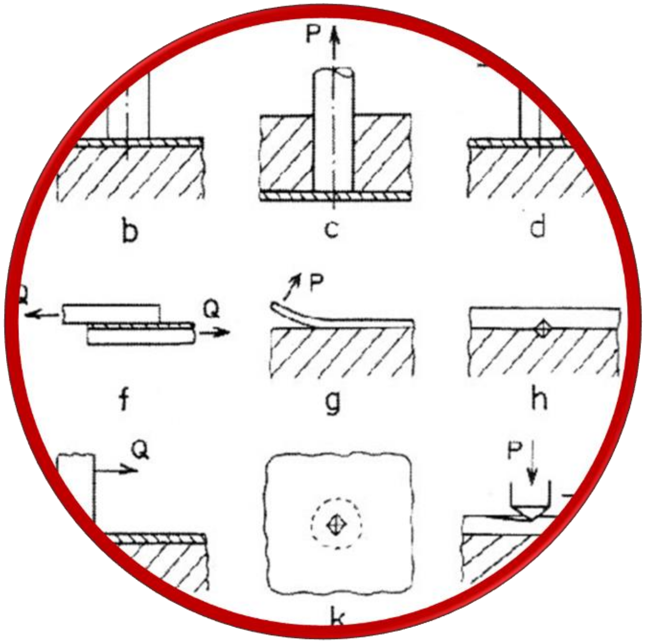
- **Mechanical properties**
  - Hardness and Young's modulus
  - 1/10 rule

- **Hard Coatings**
  - Applications & Introduction
  - Classification of hard coatings
  - Hardness and related theoretical concepts
  - Design of hard coatings

  - Nitrides and Carbonitrides
  - Carbides
  - Borides
  - Oxides

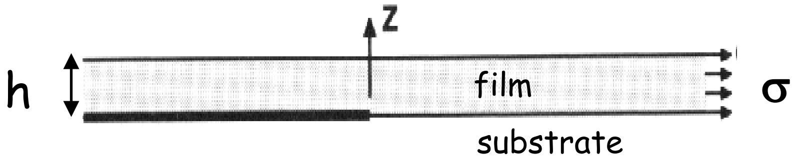
  - Multilayers & Superlattices
  - Nanocomposites
  - Cathodic Arc Plasma deposition
  - High-power impulse magnetron sputtering

Adhesion of thin films



Integral to performance and reliability of materials and materials systems are their resistance to deformation, fracture and delamination!

adhesion



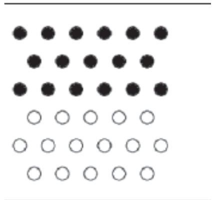
Stress intensity at crack tip

$$K = 0.7\sigma\sqrt{h}$$

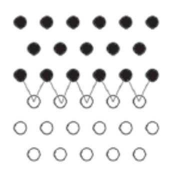
Energy release rate if interface crack propagates

$$G = 0.5\frac{1-\nu^2}{E}\sigma^2 h$$

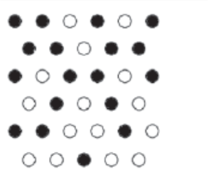
Atomistic view of interface



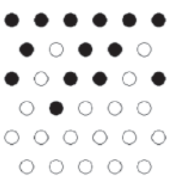
Interface without chemical bonding



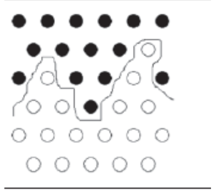
Interface with chemical bonding



Transition zone through diffusion (danger of formation of porosity due to Kirkendall effect)

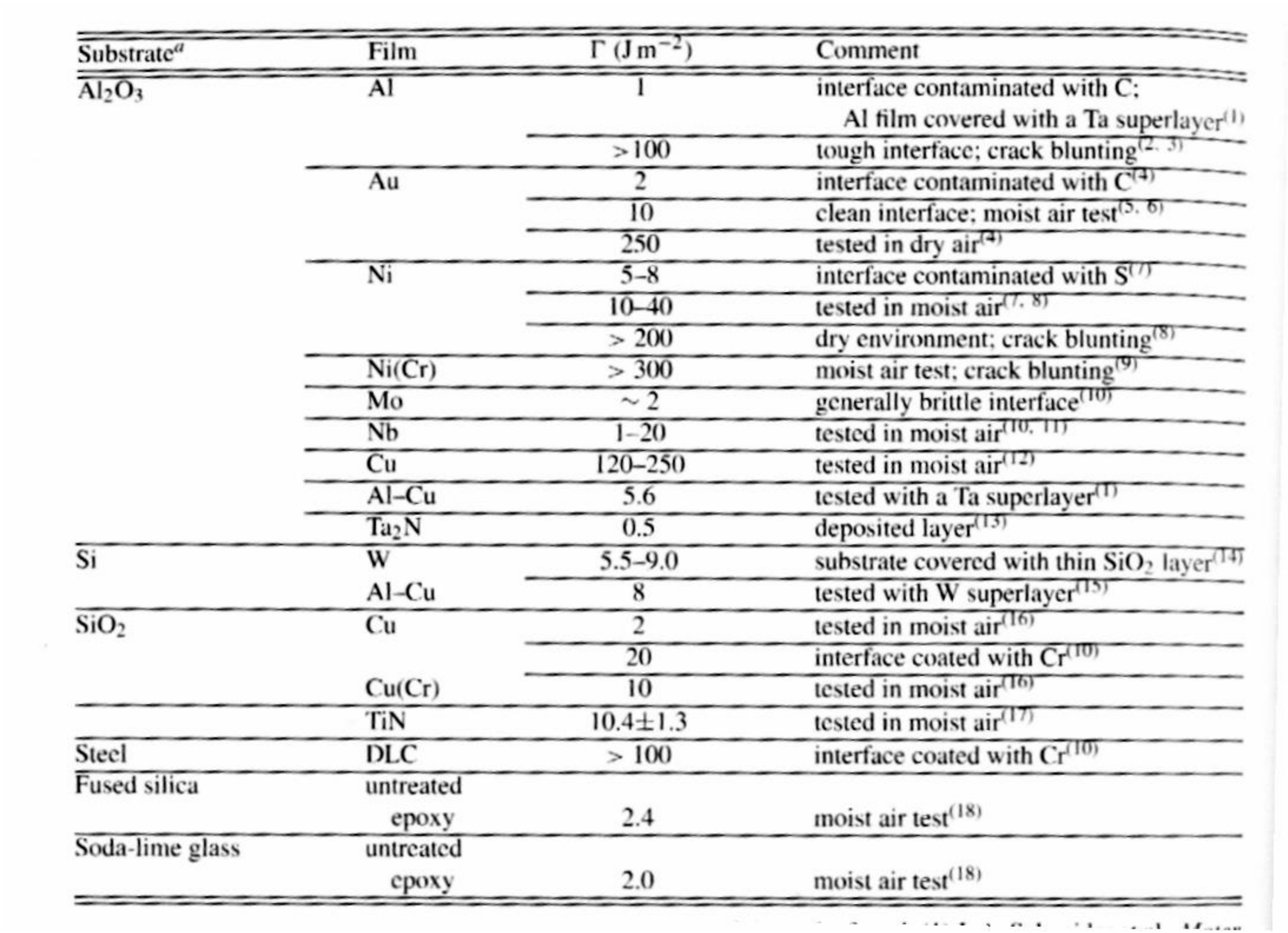


Interface mixing due to ion bombardment



Interface transition zone due to mechanical locking

Interface fracture toughness



Substrate[a]	Film	Γ ($J\,m^{-2}$)	Comment
Al_2O_3	Al	1	interface contaminated with C; Al film covered with a Ta superlayer(1)
		>100	tough interface; crack blunting(2, 3)
	Au	2	interface contaminated with C(4)
		10	clean interface; moist air test(5, 6)
		250	tested in dry air(4)
	Ni	5–8	interface contaminated with S(7)
		10–40	tested in moist air(7, 8)
		> 200	dry environment; crack blunting(8)
	Ni(Cr)	> 300	moist air test; crack blunting(9)
	Mo	~ 2	generally brittle interface(10)
	Nb	1–20	tested in moist air(10, 11)
	Cu	120–250	tested in moist air(12)
	Al–Cu	5.6	tested with a Ta superlayer(1)
	Ta_2N	0.5	deposited layer(13)
Si	W	5.5–9.0	substrate covered with thin SiO_2 layer(14)
	Al–Cu	8	tested with W superlayer(15)
SiO_2	Cu	2	tested in moist air(16)
		20	interface coated with Cr(10)
	Cu(Cr)	10	tested in moist air(16)
	TiN	10.4±1.3	tested in moist air(17)
Steel	DLC	> 100	interface coated with Cr(10)
Fused silica	untreated epoxy	2.4	moist air test(18)
Soda-lime glass	untreated epoxy	2.0	moist air test(18)

Strategies against bad film adhesion I – glue layers

Glue Layers

Conventional wisdom, for example, might suggests using very clean substrates to get good adhesion.

This may not necessarily work for metal films on glass substrates because optimum adhesion appears to occur only when the metal contacts the substrate through an oxide bond. Thus Al adheres better when there is some Al_2O_3 present between it and the glass substrate. It is not surprising that strong oxide formers adhere well to glass. Intermediate oxide layers can be produced by depositing metals with large heats of oxide formation such as Cr, Ti, Mo, and Ta.

Conversely, noble metals such as Au, Ag, and Cu do not form oxides readily and accordingly, adhere poorly to glass.

To promote adhesion it is common practice, therefore, to first deposit a few hundred angstroms of an intermediate oxygen-active metal to serve as the "glue" between the film and substrate.

This is the basis of several multilayer-metallization contact systems, including Ti-Au, Ti-Pd-Au and Ti-Pt-Au, Cr-Au, Cr-Pd-Au, Cr-Ag, and Mo-Au. After deposition of the intermediate glue layer, the second film should be deposited without delay, for otherwise the glue metal may oxidize and impede adhesion of the covering metal film. Added layers to improve adhesion are unwelcome because additional deposition steps are costly and often introduce new reliability problems.

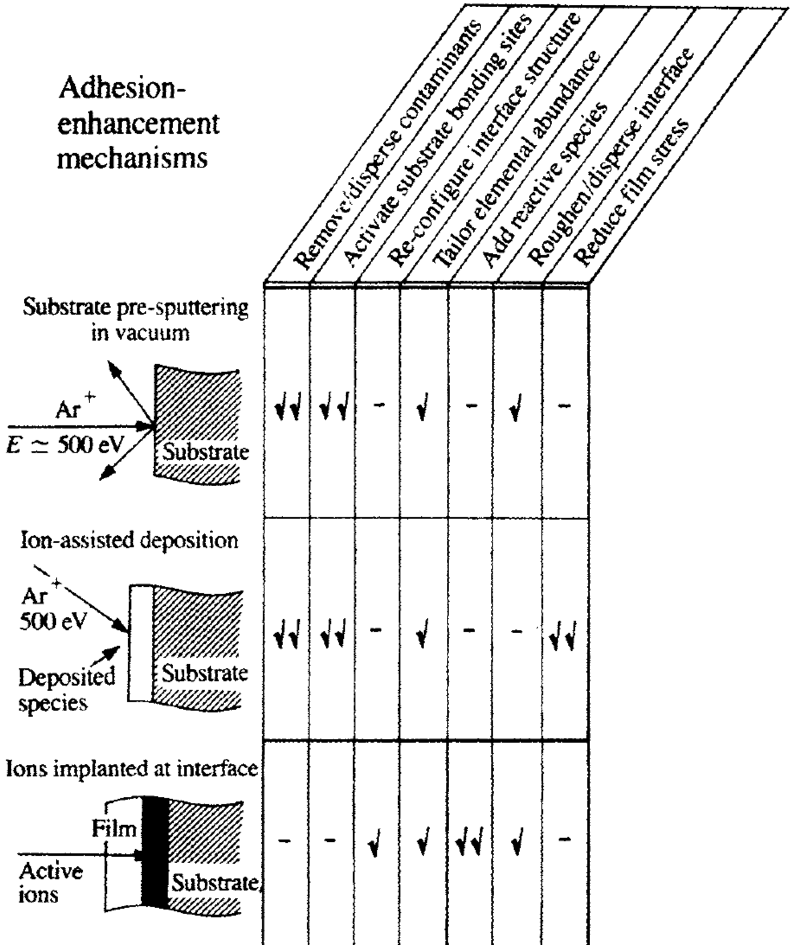
Ohring 2003

Strategies against bad film adhesion II – ion beam processing

*1. **Low-energy presputtering.*** Cleaning substrates by a presputtering treatment with ions having energies between **100 eV and a few keV** is a good way to enhance subsequent film adhesion. **This cleaning procedure** removes most contaminants including surface-bonded polymer chains, oil films, and terminal oxide layers.

*2. **Ion-beam-assisted deposition.*** In this case **ion beams with several keV energy at fluxes of 5 10^{15} ions/cm^2** accompany film deposition. Therefore, in addition to the benefits of presputtering, the **film is densified**. The interfacial "**pseudodiffusion**" layer produced is a type of structurally disordered transition zone, in which the solubility of the involved components exceeds equilibrium limits. All in all, diffusion occurs between materials that do not naturally mix or adhere.

*3. **Reactive ion implantation:*** Whereas the first two processes are carried out at low energies, ion implantation **requires an expensive accelerator**. However, there are some advantages to reactive ion implantation, including the creation of compositionally graded layers and ballistic mixing at the interface.



Adhesion-enhancement mechanisms	Remove/disperse contaminants	Activate substrate bonding sites	Re-configure interface structure	Tailor elemental abundance	Add reactive species	Roughen/disperse interface	Reduce film stress
Substrate pre-sputtering in vacuum	√√	√√	-	√	-	√	-
Ion-assisted deposition	√√	√√	-	√	-	-	√√
Ions implanted at interface	-	-	√	√	√√	√	-

Ohring 2003

Strategies against bad film adhesion III – polymers

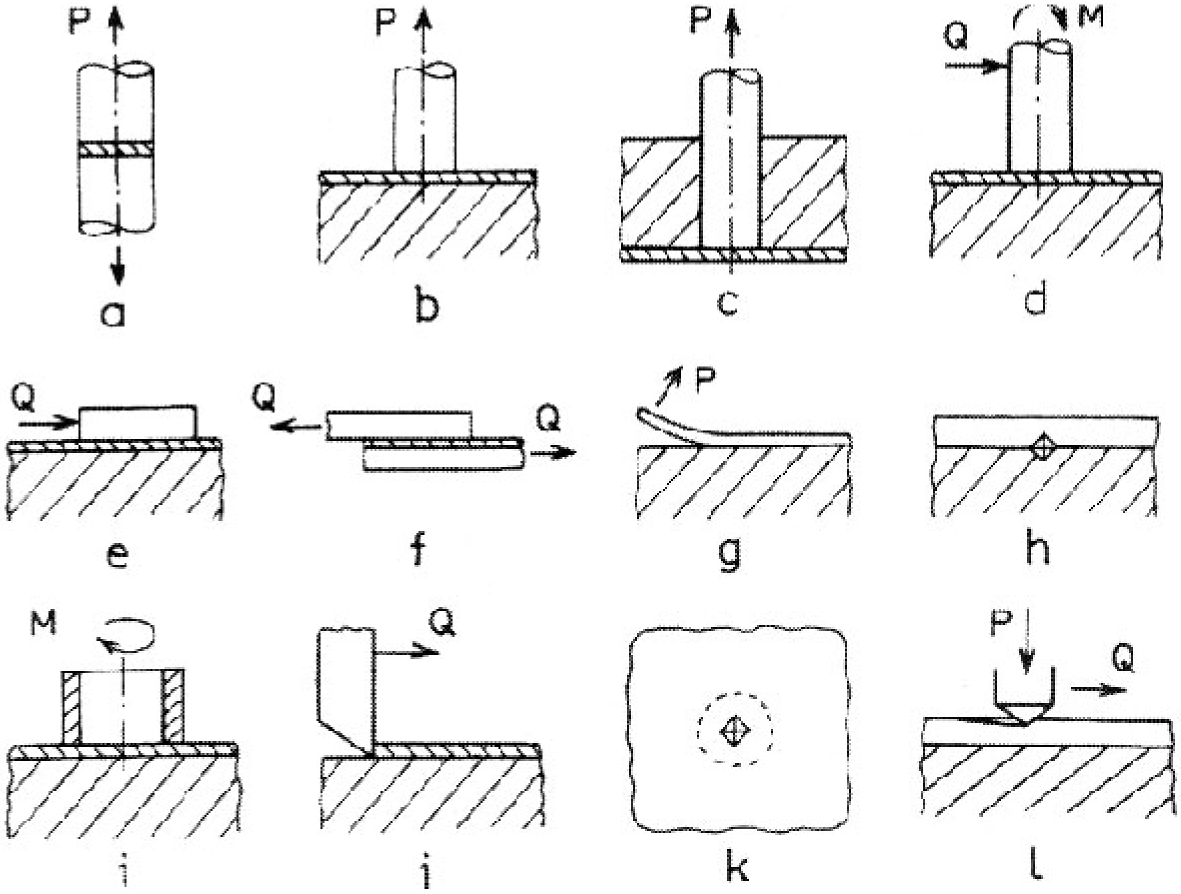
There is often a need to deposit thin metal films on polymeric substrates. This often proves a challenge because of **great differences in atomic bonding, melting points, and thermal expansion coefficients** between the involved materials.

Strategies to improve adhesion broadly attempt to modify polymer surfaces by either physical or chemical means.

Alteration of **surface topography, mechanical abrasion, and plasma treatment** of surfaces are examples of the **physical approach**. Plasmas with their collective assortment of ions, electrons, and photons enhance adhesion by removing contaminants, roughening surfaces, promoting crosslinking, and generally introducing or removing reactive chemical groups. In particular, the greater chemical reactivity of the surface often enhances nucleation of deposited films. Both oxygen and nitrogen plasmas are often employed to activate polymer surfaces.

Ohring 2003

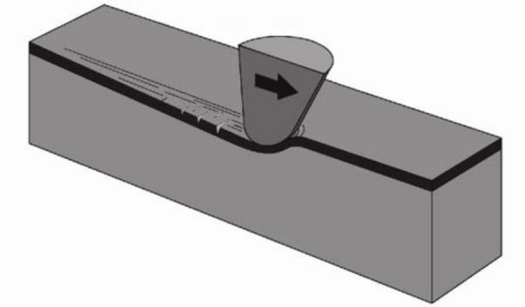
Coating adhesion testing

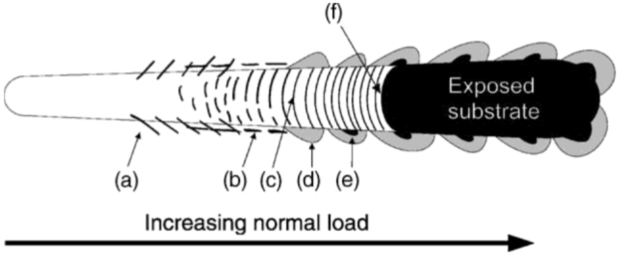


Roughly 300 different methods

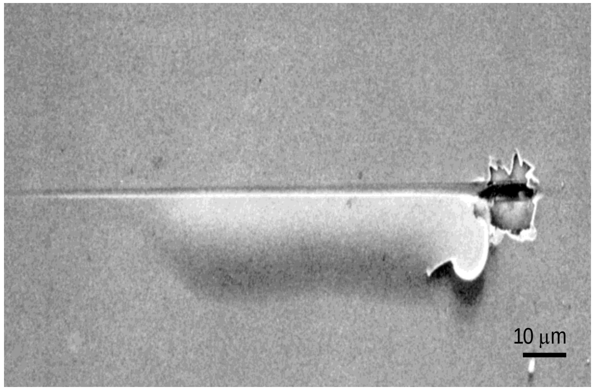
Scratch Testing

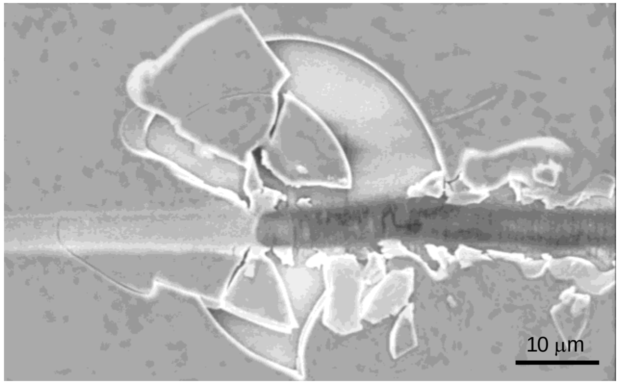
- Draw diamond tip across surface with increasing normal load until a critcal event occurs
- Film will debond (form buckle) or fracture (form through thickness cracks)





uniform width blisters

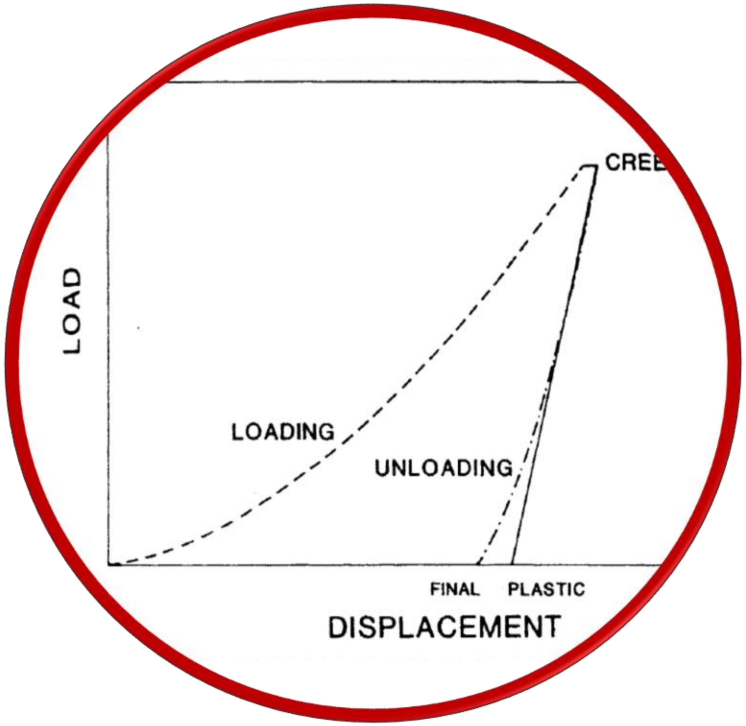




spalled blisters

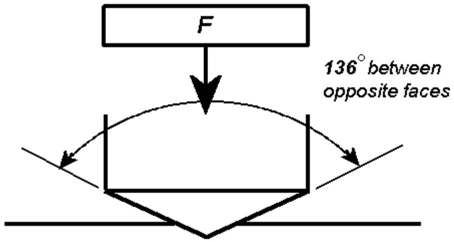
Holmberg, Laukkanen, et al, *Wear.* 254 (2003) 278.

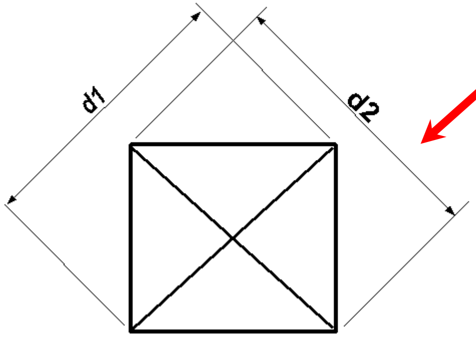
Measurement of mechanical film properties



Vickers Hardness Test

Diamond indenter body
(Vickers pyramid)





Residual impression
measured
by optical microscopy

$$HV = \frac{2F\sin\frac{136^\circ}{2}}{d^2} \approx 1.854\cdot\frac{F}{d^2}$$

Load in kgf
d in mm

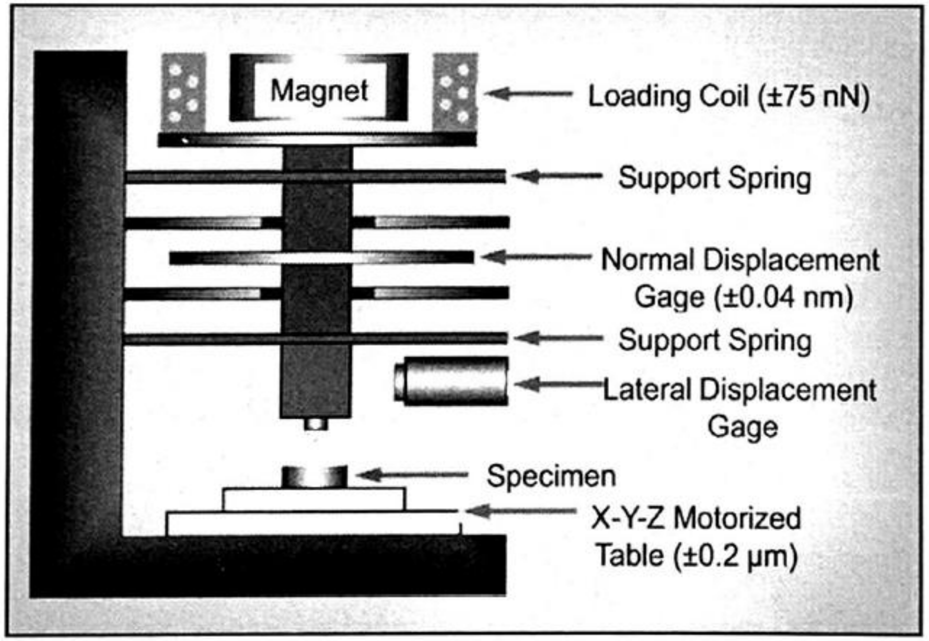
1 kgf = 9.81 N

$$HV = 0.1891\cdot\frac{F}{d^2}$$

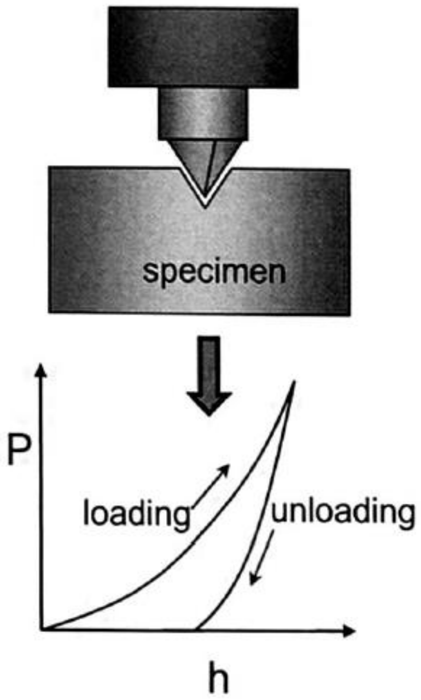
Load in N
d in mm

Advantage:	„Easy“
Disadvantage:	Operator needed for optical measurement „NOT SUITED“ FOR SMALL OBJECTS OR THIN FILMS

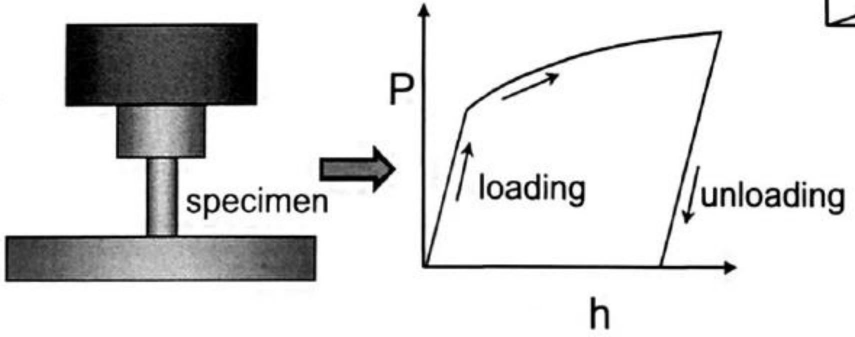
A nanoindenter

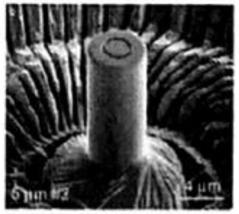


Indentation:



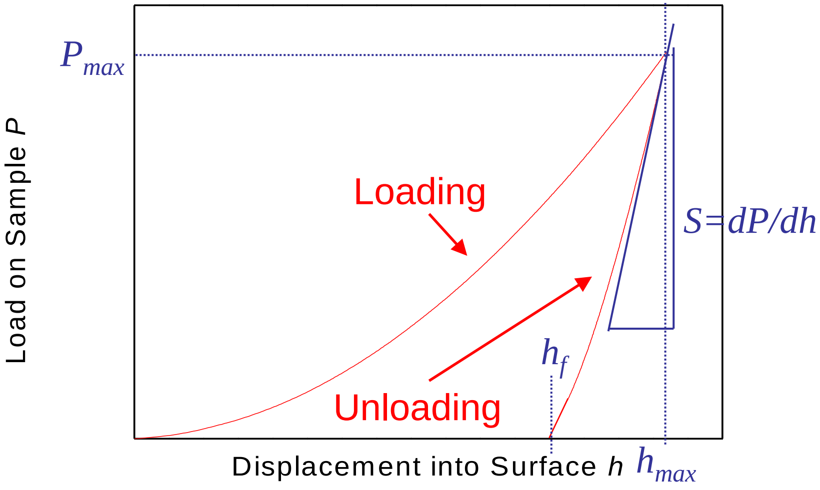
Pillar Testing:





Courtesy GM Pharr, Univ. Texas

Principle of nanoindentation



hardness:
Average contact pressure at maximum load (projected area)

Young`s modulus:
proportional to slope of unloading curve

Nanoindentation experiments on thin films

Advantage:
Film can be measured without removing it from the substrate
Spatial distribution in lateral & vertical direction

Chief difficulty:

Avoiding unintentional probing of substrate properties

Empa
Materials Science and Technology

"1/10-rule of thumb"

Rule of thumb by H. Bückle:
(h_{max} = maximal depth; d_{Film} = film thickness)

$$h_{\max} \leq 0.1 \cdot d_{Film}$$

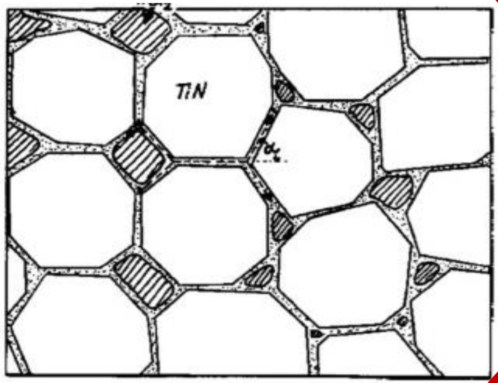
For the "extreme" cases of a hard film on a soft substrate (Nanocomposite coatings) or for a soft coating on a hard substrate (Al on glass)
this rule may be too lax or to strict

H. Bückle, VDI Berichte, Vol. 41, p. 14, 1961

Choice of applied maximal load / maximal displacement

Rules:
- Displacement > 20 R_a
- Displacement ≤ 10% of coating thickness

Hard coatings



Introduction

Hard Coatings:

Class of **thin films** characterized by extremely **high hardness**, **very high melting points**, and **resistance to chemical attack.**

Deposited on tool substrates to protect engineering components (cutting tools, dies, punches, ball bearings, gas turbines,…) from severe external loading and harsh environments.

Coatings improve desired properties such as **hardness, friction, wear- and corrosion resistance**, without changing the properties of the bulk material.

Hardness: **hard** (20 GPa $< H <$ 40 GPa) and **superhard** ($H \geq$ 40 GPa)

Typical thickness: 1 to 15 μm, deposited by different PVD and CVD methods

Classification of hard coatings:

I) Intrinsically according to the **nature of their chemical bonds** (covalent, ionic, metallic)
II) Extrinsically according to their **microstructure** (multilayers, nanolaminates, nanocomposites)

Ohring 1992

Applications

Cutting tools

Moulds for plastic processing

Engine components

Aircraft components

Textile machine components

Cutter blades

General machine parts

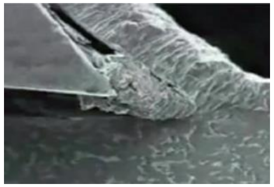
Household appliances

Drilling tools for oil/gas industry and wind turbines

Medical technology

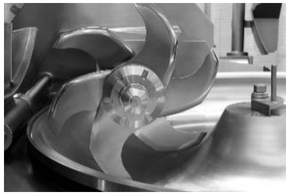
Decorative applications

DLC – coated piston pin



Cutting tools such as TiAlN

DLC-coated thread guide



Cutter blades with a CrN coating

TiN or DLC coated Aircraft landing gear

DLC coated roller bearing

LC-coated ceramic washers

TiN-coated medical instruments

rosé gold, Ti or deep black DLC

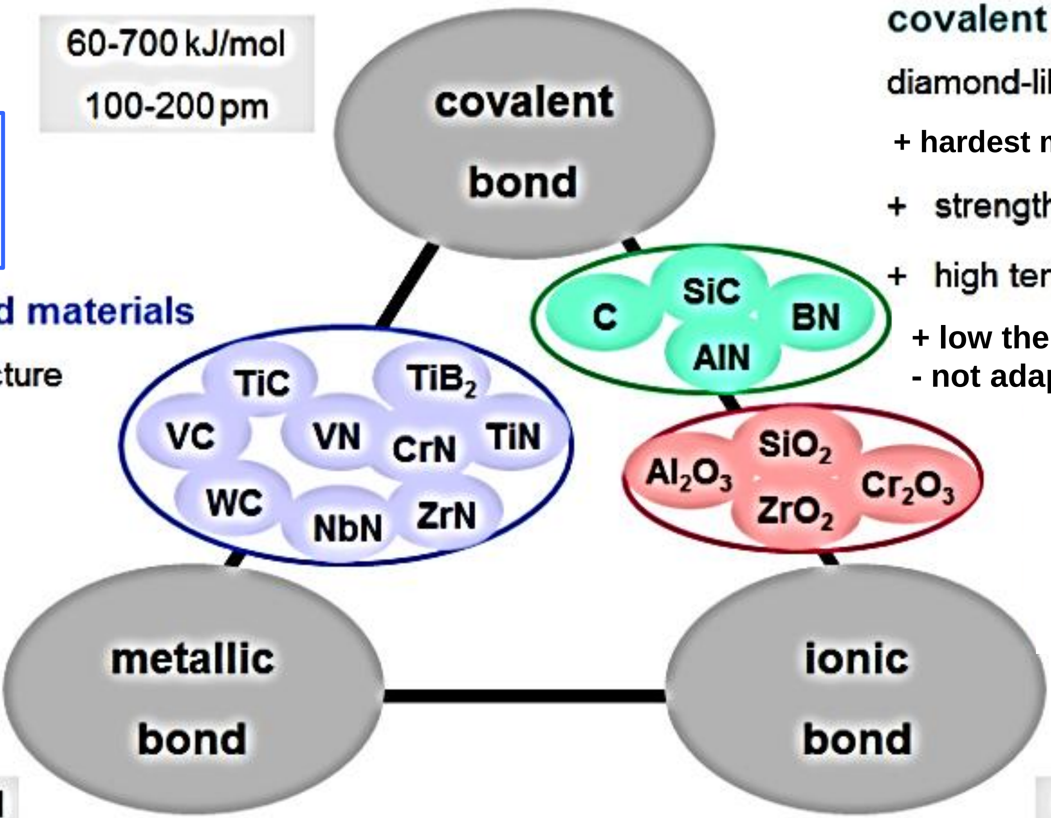
https://oerlikon-balzers.bibliothek-der-technik.de/

Classification of Hard Coatings

Three groups are distinguished based on chemical bonding.
The nature of bonding relates to specific properties characteristic of each group.

nitrides, carbides and borides of Al, Si, B; diamond

transition metal nitrides, carbides and borides



60-700 kJ/mol
100-200 pm

metallic hard materials

metal-like structure

- \+ adhesion
- \+ toughness
- \+ ductility
- \+ high elastic modulus

110-350 kJ/mol
100-200 pm

covalent hard materials

diamond-like structure

- \+ hardest materials (Diamond,c-BN)
- \+ strength
- \+ high temperature strength
- \+ low thermal expansion coefficient
- \- not adapted to metallic substrate at HT

ionic hard materials

ionic structure

- \+ hardness
- \+ thermodynamic stability
- \+ chemical inertness
- \- very brittle

600-1100 kJ/mol
up to 300 pm

hard materials: mixed bonds (covalent + metallic + ionic)

Holleck, H. in.Surface Engineering: science and Technology I. 1999.

Introduction

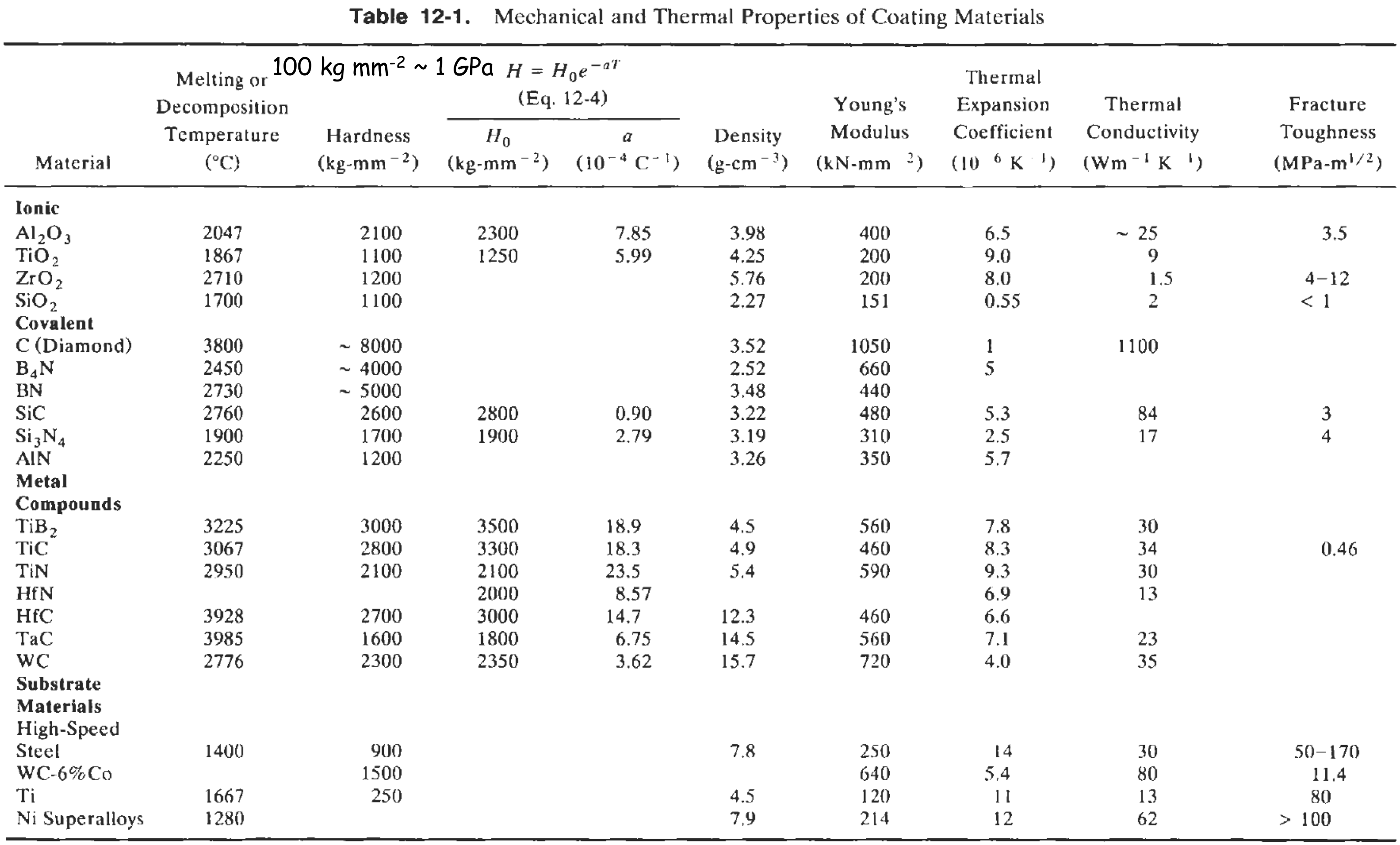


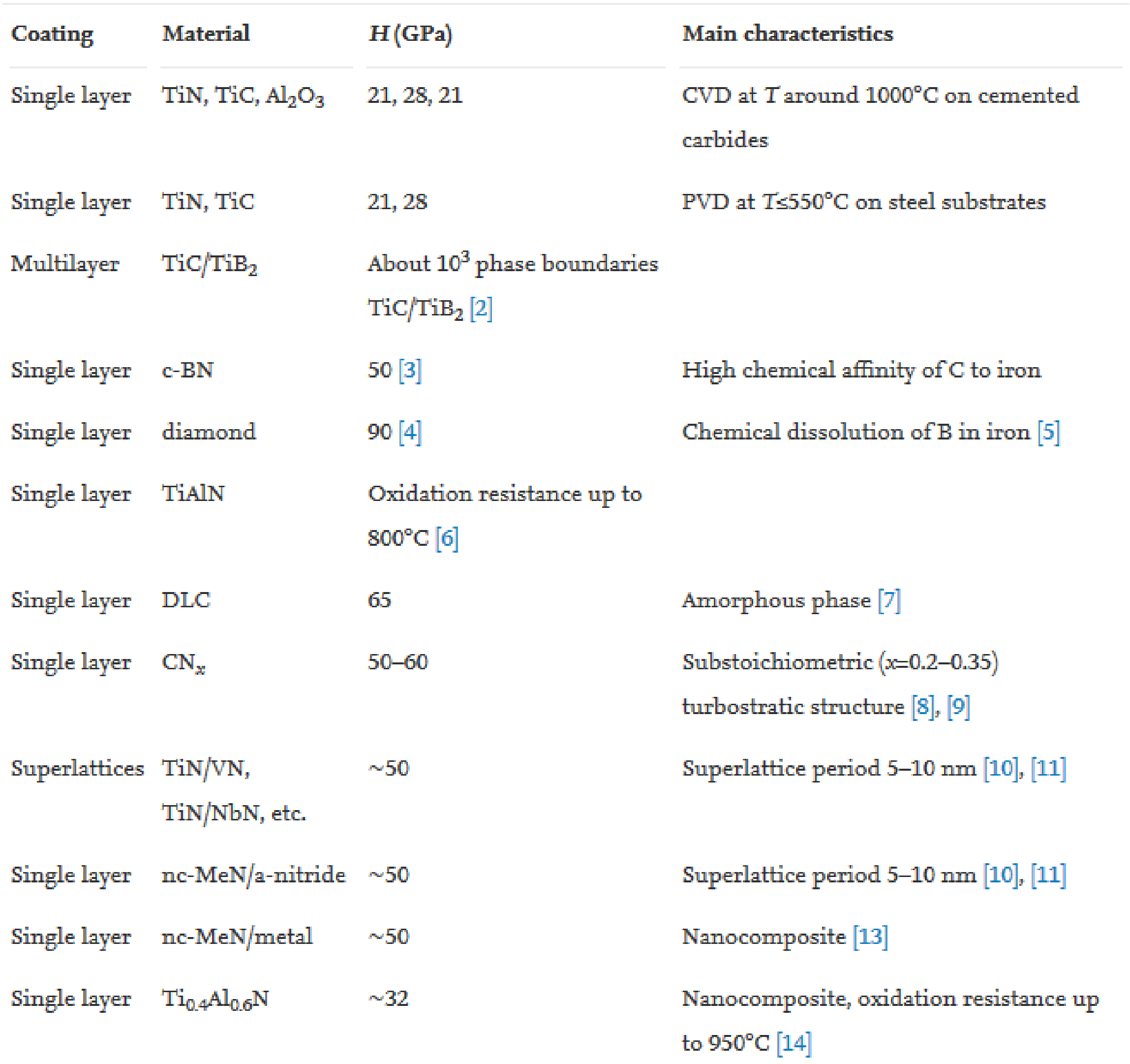
Table 12-1. Mechanical and Thermal Properties of Coating Materials

100 kg mm^{-2} ~ 1 GPa

Material	Melting or Decomposition Temperature (°C)	Hardness (kg-mm^{-2})	$H = H_0 e^{-aT}$ (Eq. 12-4) H_0 (kg-mm^{-2})	a (10^{-4} C^{-1})	Density (g-cm^{-3})	Young's Modulus (kN-mm^{-2})	Thermal Expansion Coefficient (10^{-6} K^{-1})	Thermal Conductivity (Wm^{-1} K^{-1})	Fracture Toughness (MPa-m$^{1/2}$)
Ionic									
Al_2O_3	2047	2100	2300	7.85	3.98	400	6.5	~ 25	3.5
TiO_2	1867	1100	1250	5.99	4.25	200	9.0	9	
ZrO_2	2710	1200			5.76	200	8.0	1.5	4–12
SiO_2	1700	1100			2.27	151	0.55	2	< 1
Covalent									
C (Diamond)	3800	~ 8000			3.52	1050	1	1100	
B_4N	2450	~ 4000			2.52	660	5		
BN	2730	~ 5000			3.48	440			
SiC	2760	2600	2800	0.90	3.22	480	5.3	84	3
Si_3N_4	1900	1700	1900	2.79	3.19	310	2.5	17	4
AlN	2250	1200			3.26	350	5.7		
Metal Compounds									
TiB_2	3225	3000	3500	18.9	4.5	560	7.8	30	
TiC	3067	2800	3300	18.3	4.9	460	8.3	34	0.46
TiN	2950	2100	2100	23.5	5.4	590	9.3	30	
HfN			2000	8.57			6.9	13	
HfC	3928	2700	3000	14.7	12.3	460	6.6		
TaC	3985	1600	1800	6.75	14.5	560	7.1	23	
WC	2776	2300	2350	3.62	15.7	720	4.0	35	
Substrate Materials									
High-Speed Steel	1400	900			7.8	250	14	30	50–170
WC-6%Co		1500				640	5.4	80	11.4
Ti	1667	250			4.5	120	11	13	80
Ni Superalloys	1280				7.9	214	12	62	> 100

Ohring 1992

Introduction

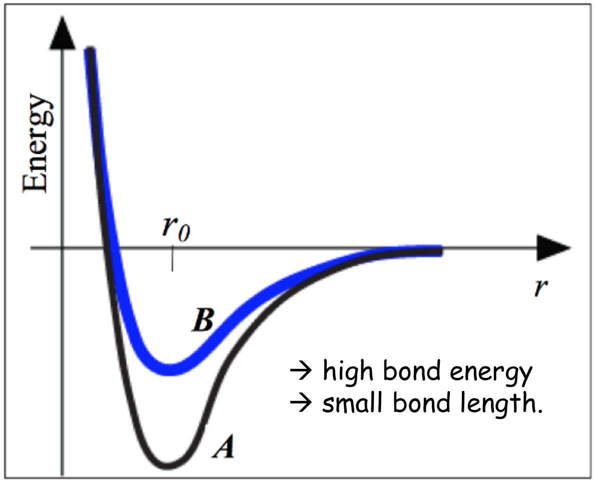


Coating	Material	*H* (GPa)	Main characteristics
Single layer	TiN, TiC, Al_2O_3	21, 28, 21	CVD at *T* around 1000°C on cemented carbides
Single layer	TiN, TiC	21, 28	PVD at $T \le 550$°C on steel substrates
Multilayer	TiC/TiB_2	About 10^3 phase boundaries TiC/TiB_2 [2]	
Single layer	c-BN	50 [3]	High chemical affinity of C to iron
Single layer	diamond	90 [4]	Chemical dissolution of B in iron [5]
Single layer	TiAlN	Oxidation resistance up to 800°C [6]	
Single layer	DLC	65	Amorphous phase [7]
Single layer	CN_x	50–60	Substoichiometric (x=0.2–0.35) turbostratic structure [8], [9]
Superlattices	TiN/VN, TiN/NbN, etc.	~50	Superlattice period 5–10 nm [10], [11]
Single layer	nc-MeN/a-nitride	~50	Superlattice period 5–10 nm [10], [11]
Single layer	nc-MeN/metal	~50	Nanocomposite [13]
Single layer	$Ti_{0.4}Al_{0.6}N$	~32	Nanocomposite, oxidation resistance up to 950°C [14]

Musil 2000

Theoretical concept of hardness

- High **intrinsic hardness** related to:
  - a high binding energy (bond strength)
  - a short interatomic distance (small bond length)
  - a high degree of directional covalent bonding (ionicity and metallicity decrease hardness)
  - a high number of valence electrons per atom
  - a high number of bonds per unit volume



→ high bond energy
→ small bond length.

- Information about intrinsic hardness in **interatomic potential**!
- Search for ultra-hard materials supported by density functional theory (DFT) calculations (maximum possible)
- Similar to theoretical strength, crystal defects and microstructure influence actually hardness values.

.

Design Parameters

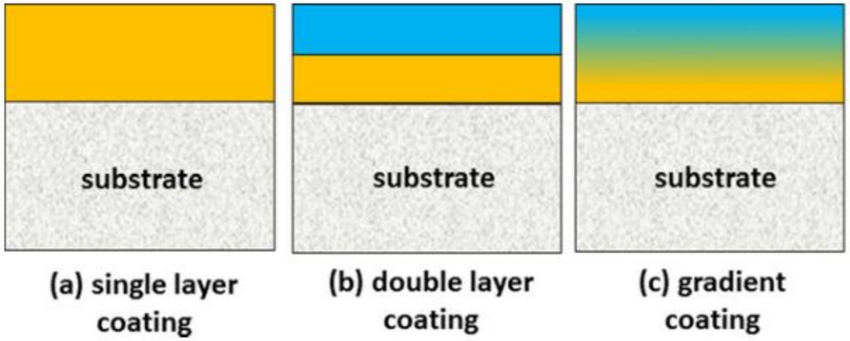
Hardness is not the only mechanical property to be considered
Some important parameters to be considered include:

- intrinsic hardness of the selected material (= the resistance to plastic deformation)
- hot hardness (hardness at working temperature of the tool)
- toughness (= the ability to absorb energy up to fracture) !
- adhesion to the substrate
- cohesion between different phases in the case of multi-phase coatings
- the residual stress in the deposited film (e.g. crack retardation by compressive stress)
- interactions with the substrate (inertness against workpiece material, low solubility)
- interaction with the environment in the chosen application (chemical stability, oxidation resistance)
- friction coefficient

- → no material can fulfill all requirements!
- → often the combination of different materials is required!

Design of Hard Coatings

The hard materials can be combined to form nanostructured coatings with e.g. enhanced hardness, toughness and oxidation resistance



Double layer coating: properties of different materials can be combined.

→ adjust elastic properties and thermal expansion of the top layer to those of the substrate material

e.g. bottom layer: high hardness (high wear resistance)
relatively soft top layer: low friction coefficient & corrosion resistant

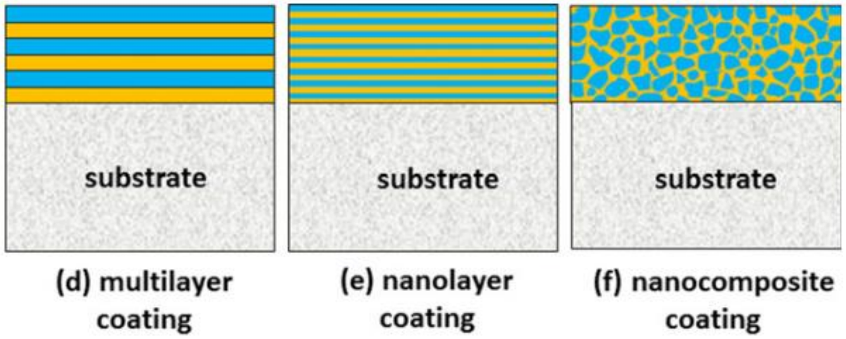
Gradient coating: can be used as an alternative to two discrete layers

Example: **TiCN coating**, in which the ratio between carbon and nitrogen atoms changes during deposition process.

H. Caliskan et al., Comprehensive Materials Finishing, 2017

Design of Hard Coatings

The hard materials can be combined to form nanostructured coatings with e.g. enhanced hardness, toughness and oxidation resistance



→ Superhard coatings, higher hardness than conventional coatings

Multilayer coating: double layer structure repeated several times. Hardness follows typically rule of mixture.

Nanolayer coating: individual layer thickness < 10 nm , the total number of layers increases to several hundred. Hardness well beyond rule of mixture due to size effects.

Nanocomposite: two-phase structure is formed during deposition. One phase segregates to the grain boundary of the second phase. The size of the grains is in the nanometer range. Hardness beyond rule of mixture.

Example: Nanocrystalline TiN embedded in amorphous SiNx

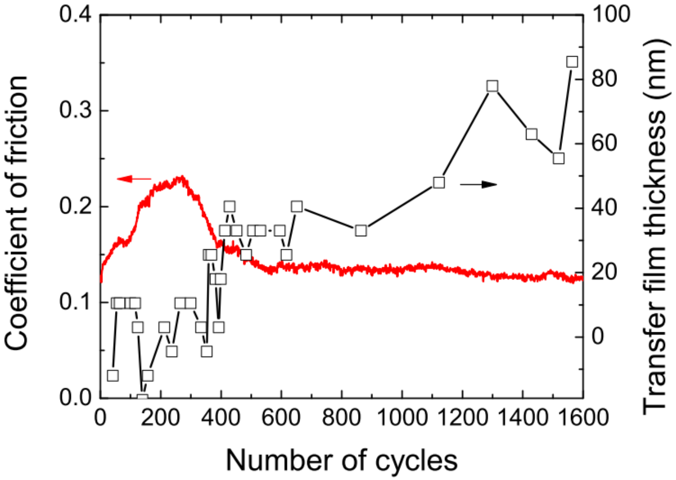
H. Caliskan et al., Comprehensive Materials Finishing, 2017

Nitrides and Carbonitrides I

Coatings based on **transition metal nitrides** like the face-centered **cubic (fcc) TiN**, deposited by CVD (1970) or PVD (1980) have been the **first to be commercially applied** for the reduction of tool wear in machining operations up to 1000°C.

To enhance the abrasion and erosion resistance of **TiN** (which is still often the standard coating used for a huge variety of applications), ***carbon is added at the expense of nitrogen***. This results in the formation of a stable solid solution **TiC_xN_{1-x}**.

Coefficient of friction and transfer film thickness of TiC_xN_{1-x} versus number of cycles in a sliding test against Al_2O_3, Rebelo de Figueiredo et al., 2010



golden-yellow TiN coating

TiC_xN_{1-x} is also has **excellent friction properties.** The friction coefficient against alumina (TiN 0.6–0.8) is reduced to approximately 0.2. This is related to the *in situ* formation of **self-lubricious reaction layers** after a short running-in period in dry sliding contacts. Carbon released from the coating forms an easy shearable, a few nanometer thick reaction layer in humid environment.

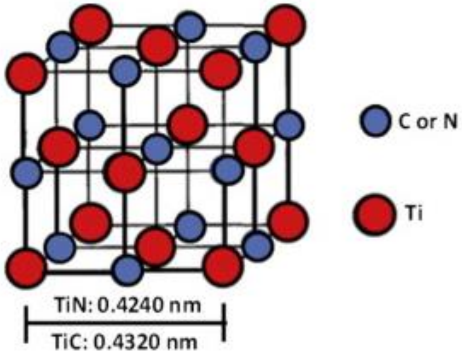
Example for a *smart, self-adaptive coating with multifunctional properties*, combining **wear resistance and low friction**.

https://robbjack.com/support-article/tin-titanium-nitride-coating/

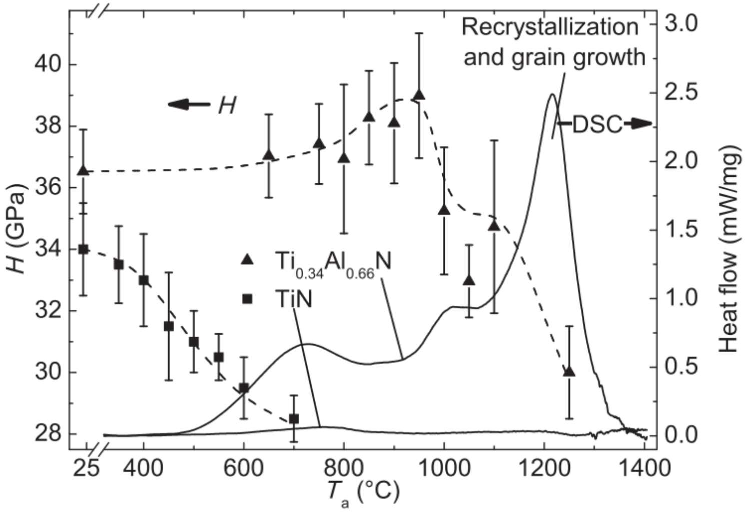
Nitrides and Carbonitrides II

$Al_xTi_{1-x}N$ introduced (1980). Al replaces Ti in TiN forming a **metastable fcc $Al_xTi_{1-x}N$** solid solution.

Superior **oxidation resistance:** formation of a **dual-layer protective oxide scale**, with a **dense α-Al_2O_3-rich top layer** and a rutile-type **TiO_2-rich layer underneath**. Oxidation onset $T_{ox.}$ could be shifted from ~550 C for TiN (500 for TiC_xN_{1x}) to ~700 C for $Al_xTi_{1x}N$.
$Al_xCr_{1-x}N$: stable and protective α-Al_2O_3-rich and Cr_2O_3-rich layers are formed in oxidative environments ($T_{ox.}$ > 1000°C).



Metastable solid solutions undergo spinodal decomposition and **age hardening** at elevated temperatures. $Al_xTi_{1x}N$ decomposes in fcc TiN and fcc AlN domains between 700 and 900 °C, giving rise to a hardness increase due to coherency strains.



Mayrhofer et al 2003

For higher annealing temperatures, **overaging** with a coarsening of these domains and transformation of the fcc AlN into the stable hexagonal wurtzite-type AlN phase, as evidenced by differential scanning calorimetry (DSC), results in a **loss of hardness**.

Thermal stability: addition of Zr, Hf, Ta to replace Ti atoms
Oxidation resistance: low contents of Si and B → formation of protective oxide scales

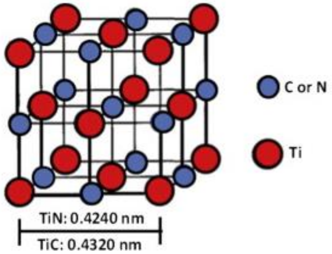
Carbides

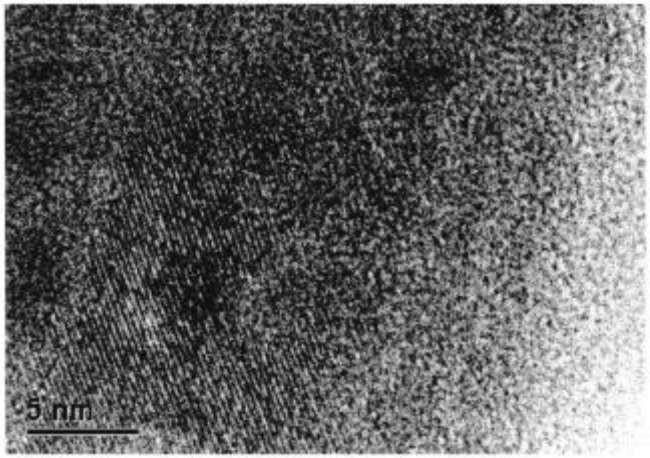
TiC was the CVD coating dominating the coating market in the early 1970s due to the **higher hardness** compared to TiN, which is a consequence of its **more covalent bonding** characteristics.

Essential **drawback** of CVD TiC coatings: large amount of the carbon needed is also supplied from the cemented carbide substrate. This results in *decarburization* and formation of a ***brittle*** *phase* in *surface-near zones of the* ***substrate***.

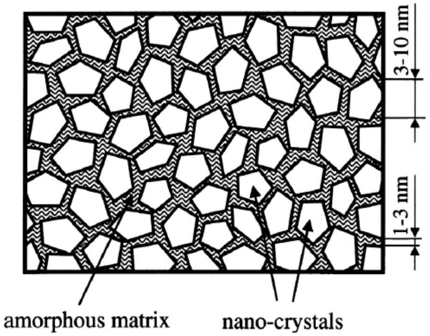
TiC coatings have thus been widely substituted by TiC_xN_{1-x}. In particular for carbon to metal ratios exceeding 1, a nanocrystalline dual-phase structure of the respective transition metal carbide plus a carbon modification is formed for both TiC and TiC_xN_{1-x}. The properties of these coatings are essentially dominated by the bonding within the carbon phase and its morphological arrangement, for example, in a **nanocomposite structure**.

“NaCl” structure



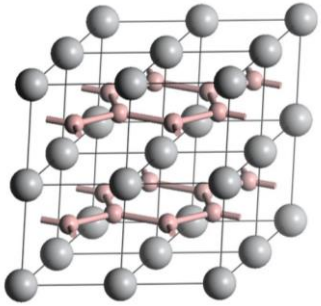


HRTEM of a nanocomposite **nc- TiC/a-C:H** coating.
Phase composition: 84 % TiC, 16% a-C:H,
Zehnder et al (J. Appl. Phys 95, 4327 (2004)

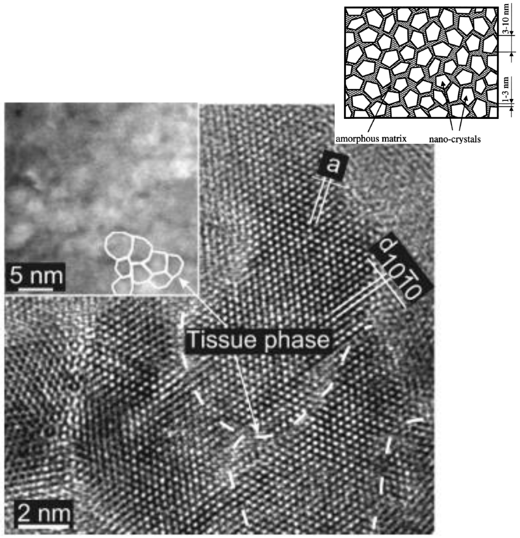


Borides

The structure of **borides** is governed by **covalent B–B bonds**, resulting in a higher bond strength and consequently hardness (> 40 GPa), elastic modulus, and melting temperature (unlike MeN/MeC with their dominating metallic binding character).

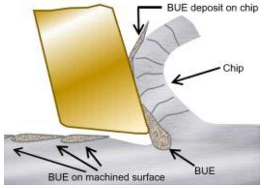


Hardness values are well above those of bulk TiB_2 (approximately 34 GPa) and have been related to a nanocolumnar structure formed by self-organization in sputtered overstoichiometric TiB_{2+x}. Such structures are often found in sputtering from TiB_2 targets due to the different scattering probabilities of Ti and B atoms during the transport from the target to the substrate.



Columns with a (0001) preferred orientation of the hexagonal TiB_2 phase and diameters of ~ 20 nm are encapsulated in the excess B. The columns themselves are composed of bundles of coherent ~ 5 nm diameter TiB_2 subcolumns, separated by a disordered 1–2 monolayers thin B-rich tissue phase. Mayrhofer et al. 2005

TiB_2 coatings are used for machining of aluminum alloys due to high hardness and chemical inertness against Al, which has a pronounced adhesion tendency to nitride coatings in cutting applications, forming build-up edges.



https://www.youtube.com/watch?v=uwh3ouvzSLk

Oxides

Among the oxides, **Al_2O_3** is dominating as a wear-protective coating for cutting tools, due to its unique combination of **chemical inertness, thermal stability, and hot hardness**.

Polymorphism: Beside the **stable hexagonal α-Al_2O_3** (also denoted as corundum, sapphire, or α-alumina), several **metastable polymorphs** (γ, δ, κ, η, θ, χ) and amorphous phases exist. The phase formed is determined by the **deposition process itself and its parameters**, with α- and κ-Al_2O_3 usually being synthesized by CVD and γ-Al_2O_3 by PVD processes.

Essentially, the **substrate temperature** and the application of **seed templates** determine the formation of these polymorphs. Typically, below a deposition temperature of 800 °C in CVD amorphous Al_2O_3 is formed. Most often, a TiC_xN_{1-x} **base layer** is used in CVD, to provide the necessary adhesion of the Al_2O_3 top layer.

Transformation of the orthorhombic κ -Al_2O_3 into the stable α-Al_2O_3 modification occurs at a temperature of approximately 1000 ° and results in **coating cracking and delamination** due to the associated volume change.

The **PVD** of Al_2O_3 coatings is **still a challenge**, mainly due to their **electrically insulating nature**, requiring pulsed d.c. or r.f. plasmas. At low deposition temperatures, coatings are reported to be X-ray amorphous. Between 350 and 550 °C, crystalline cubic γ -Al_2O_3 is grown, the desired α-Al_2O_3 modification requires 700 °C.

To exploit α-Al_2O_3 as a wear-protective coating on high-speed steel cutting tools, deposition **temperatures below 600 °C** are required to avoid **softening of the substrate**. The most efficient **template or stabilizer** for α-Al_2O_3 growth known up to now is Cr_2O_3, which is isostructural with corundum (synonym to α-Al_2O_3).

Mitterer 2014

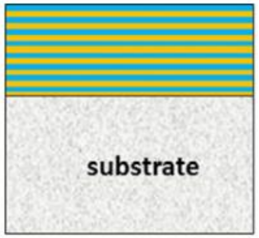
Nanostructured coatings

→ Different mechanisms can lead to the hardening of a crystalline material, mainly acting by **hindering or the retarding the deformation generated by dislocation movements**.

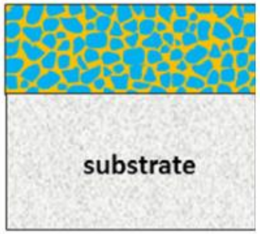
→ additionally toughness, thermal stability and oxidation resistance are enhanced through microstructural design

Hard nanostructured coatings can be divided into two main classes:

- **Hard multilayers/nanolayers/nanolaminates** (and **superlattices**), with a composition and phase modulation in one direction of space i.e. the growth direction
- **Hard nanocomposites**, the structure of which is modulated in all three direction of space, with a characteristic length at the nanometer scale



(e) nanolayer coating



(f) nanocomposite coating

Nanostructured Hard Coatings - Multilayers

In multilayered and superlattice films two or more nanometer thick layers of different materials are periodically alternated to produce a total film thickness of several micrometers.

Formation of dislocation and nanocracks and their propagation is strongly prohibited, similar to nanocrystalline materials with strong boundary regions.

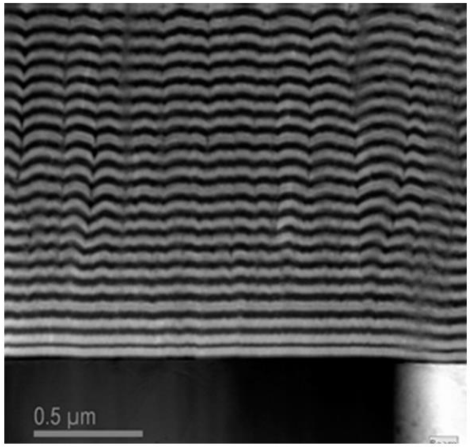


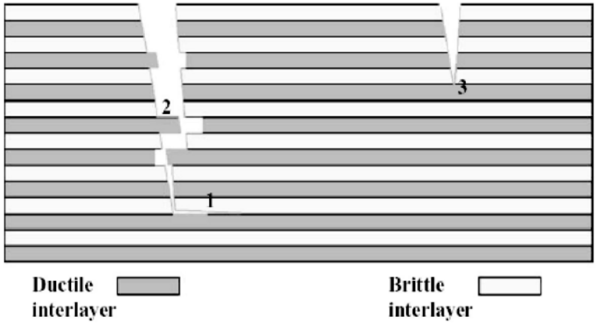
Figure 2 SEM image of CrN/TiAlN layers deposited on a steel substrate.

Typical toughening mechanisms observed in multilayer films :

- crack deflection at interface between layers,
- ductile interlayer ligament bridging and crack tip blunting
- interface delamination

All cause **extra energy consumption** and dissipation during crack propagation.

These effects can be even enhanced if materials with high and low elastic properties are used. Dislocations cannot be transmitted across individual layers since they need to overcome very high repulsive image stresses.



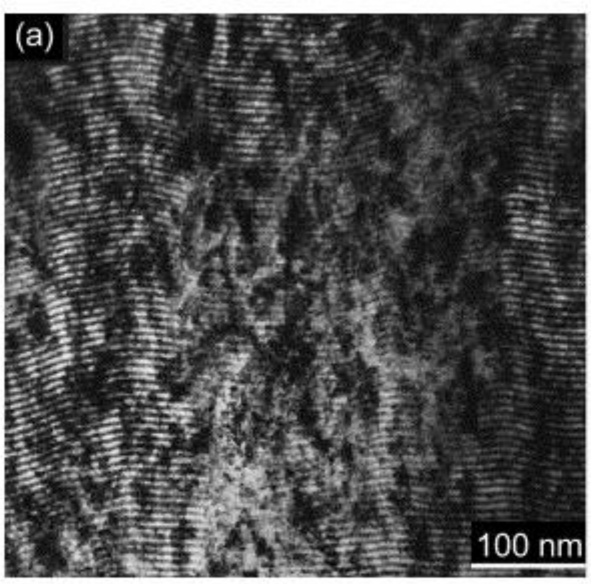
1) Crack deflection
2) Ductile interlayer bridging
3) Crack tip blunting

Superlattices

Heteroepitaxial multilayer structure with an individual layer thickness of nanometer scale.

Source of hardening: high number of interfaces, different shear moduli & coherency strains

Typical maximum hardness and toughness obtained at 5–10 nm bilayer period thickness.



TiN/NbN multilayer
Modulation period 7.2 nm
Mayrhofer et al 2006

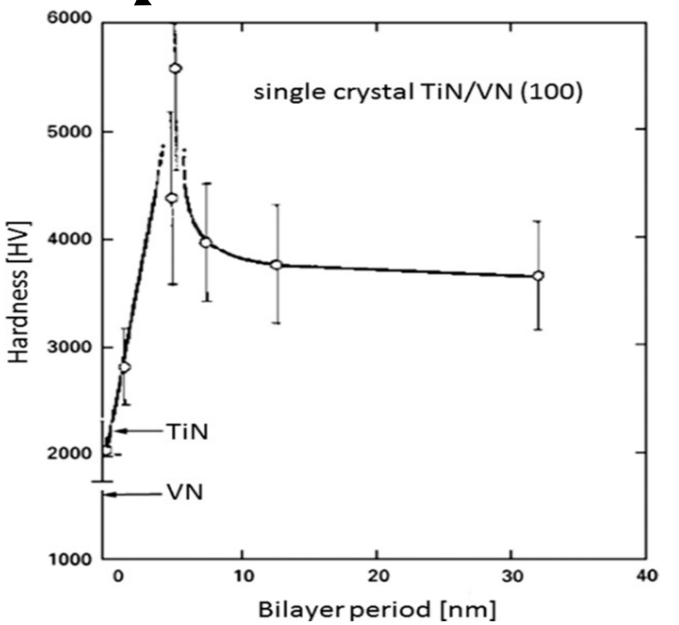


Figure 4 Hardness change of nanolayer TiN/VN coating as a function of bilayer period.[37]

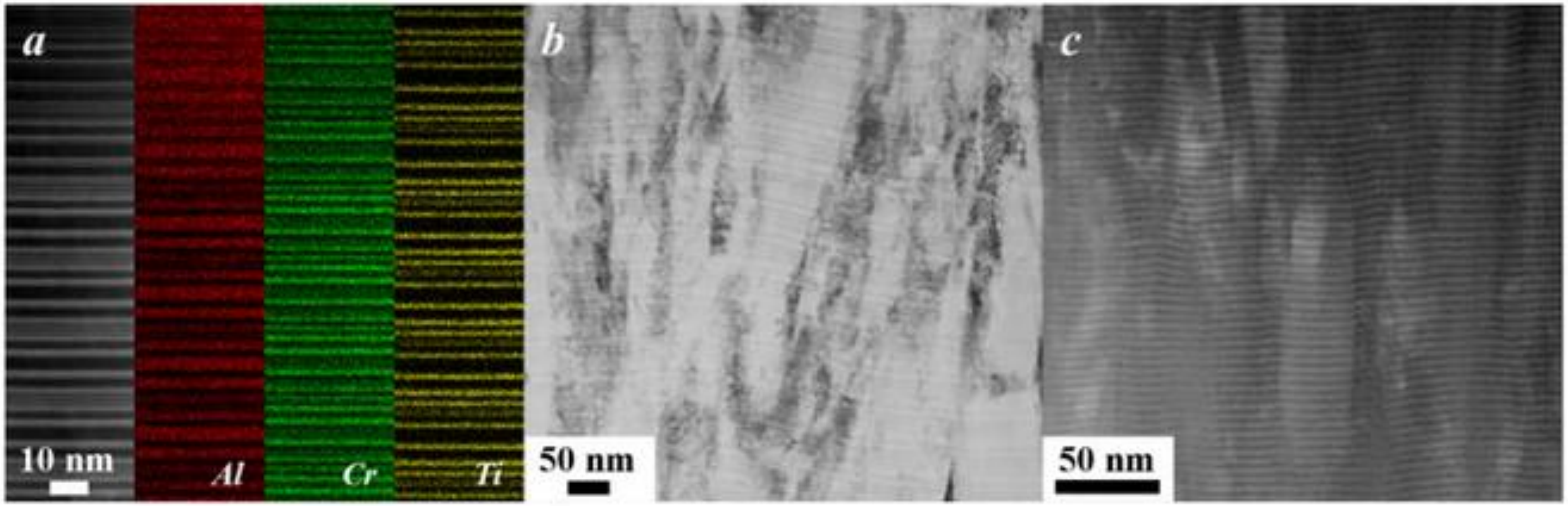
Caliskan et al 2017

More complex Nanolaminates

DF-STEM & EDX

BF-STEM

DF-STEM



$TiN/AlCr_{30}N/CrN/AlN$

$AlSi_{18}N/CrN/AlCr_{30}N/CrN$

$TiN/AlTi_{33}N/AlTi_{33}N/AlN$

Best et al. 2019

grain growth through the nano-layers.

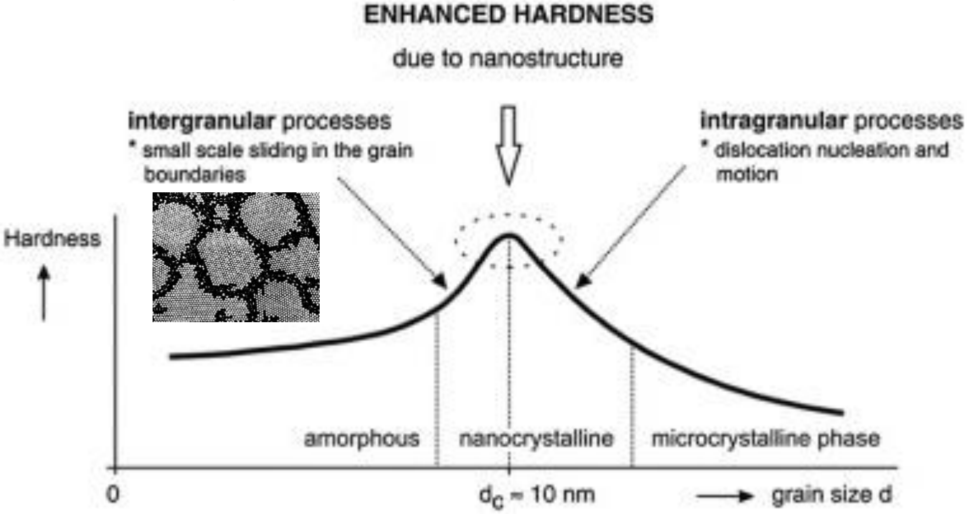
Nanostructured hard coatings – Nanocomposites I

Nanocomposites composed of at **least two separated phases** with a **nanocrystalline** and/or **amorphous structure**. The formation is principally attributed to a **segregation** of one phase **to the grain boundaries** of the second phase. This effect is hindering grain growth and forms the structure in the nanometer scale.

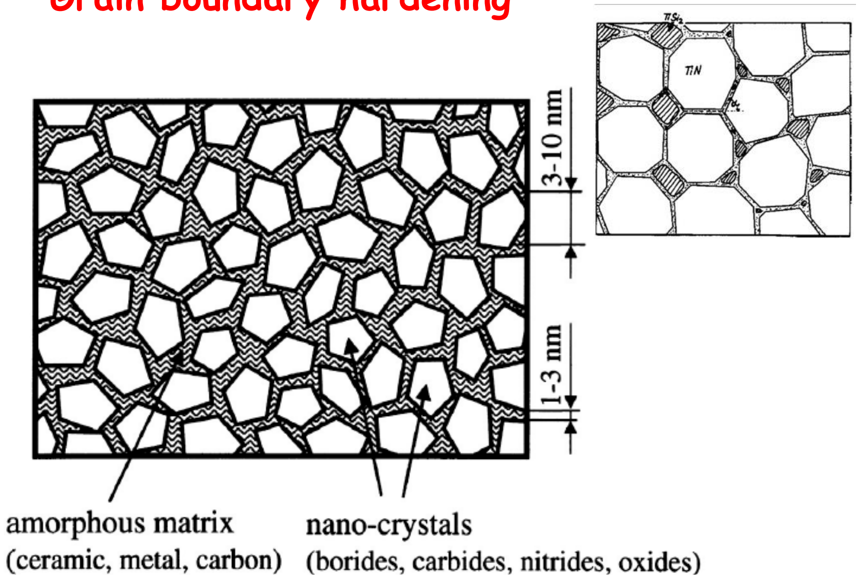
Hardening mechanism: **Grain refinement** + **Grain boundary hardening**

H_0 …intrinsic hardness
d… grain size
k… constant for a given material

$$H = H_0 + kd^{-0.5}$$



- Hall Patch equation governs coarse-grained materials (d > ca. 30 nm).
- Maximum hardness is achieved when d is close to ca. 10 nm.
- Below grain boundary sliding becomes dominant as a large fraction of atoms is located at interfaces
  → inverse or reverse Hall–Petch effect.

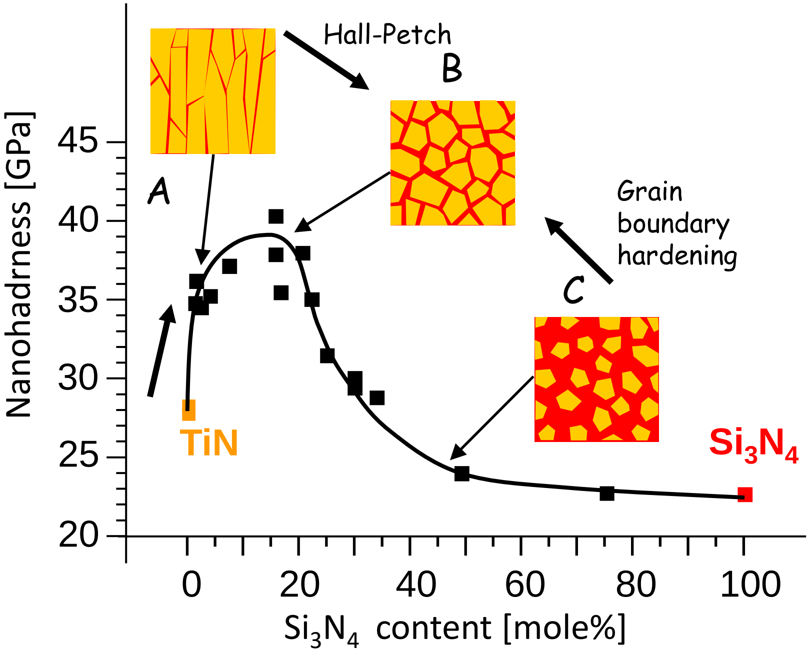


- Further hardening via **grain boundary strengthening**
- **Very small grains (≤ 10 nm)** separated by second, mainly amorphous phase
- Highest hardness > 40 GPa when separating tissue is only a few monolayers (1-3 nm)
- plastic deformation of the tissue phase by grain boundary sliding is limited

Nanocomposites II: TiN/Si_xN_y

Simultaneous evolution of nanohardness and coating microstructure as a function of Si content

A: Hardness increases due to grain refinement induced by the introduction of a-Si_3N_4



B

Hardness maximum is located in relatively small range of silicon concentration. Dislocation activity is hindered in grains < 10 nm. Thin Si_3N_4 (1-4 monolayers) prevents grain boundary sliding

C

Propagation of nanocracks in a-Si_3N_4 progressively becomes the dominant process. Hardness reaches values of pure Si_3N_4 phase

Two main groups of nanocomposite films:

- **nc-MeN(C,B,O) / hard phase** (e.g. SiN_x) is composed of **two hard phases**
- **nc-MeN(C,B,O) / soft phase** composed of **one hard and one soft** phase (e.g. Cu, Ni, Fe, Mo, Y, Ag, Co etc.)

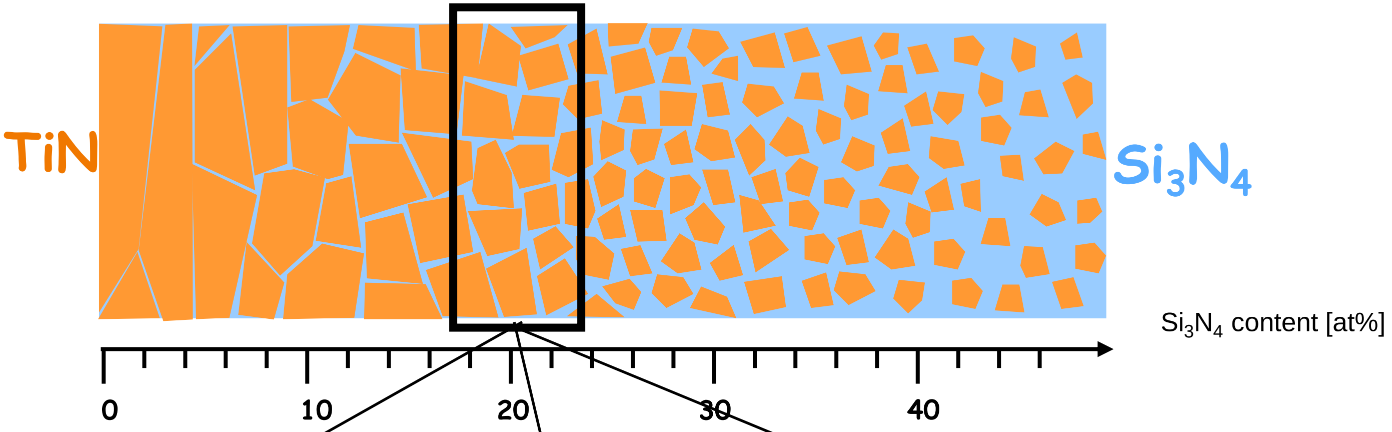
(Me =Ti, W, V, Zr, Cr,[Ti1−xAlx], [Cr1−xAlx], [Zr1−xAlx], etc.)

Courtesy of J. Patscheider, Empa

TiN/Si_xN_y nanocomposite coatings

The nanostructure is a consequence of composition and process conditions
Principle: small crystalline grains + strong boundaries

Overall properties:



High hardness
above 30 GPa
due to the nanostructure

Nanostructure is **thermally stable up to 950°C**

Oxidation resistant
by encapsulation with Si_4N_3
20 x better than TiN

Improvement of thermal stability by addition of various phases may result in reduction of hardness or other mechanical properties.

Include elements or phases of high thermal stability that hinder grain growth for a stable film structure

Courtesy of J. Patscheider, Empa

Arc plasma deposition

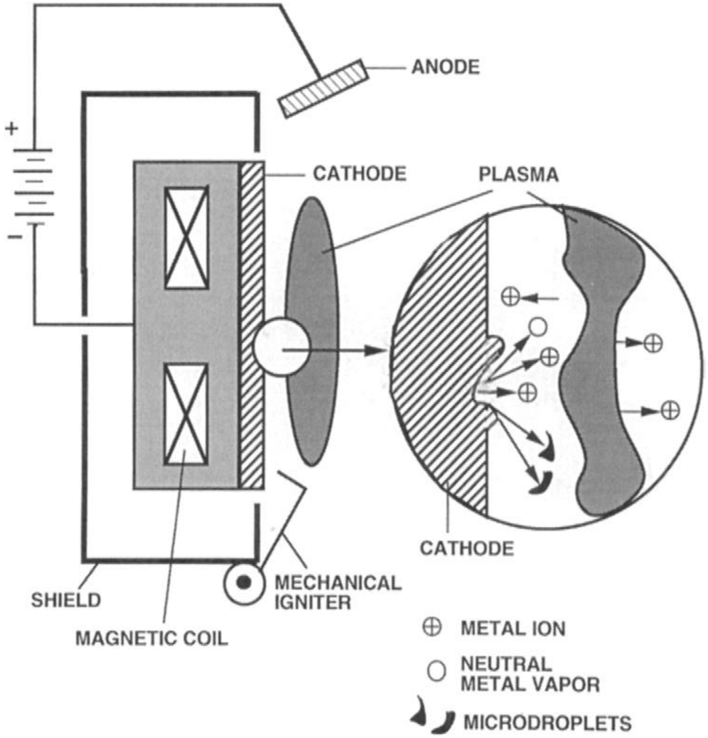
Arcs are **high-current** (tens to hundreds of amps),
low DC voltage (tens of volts) gas discharges.

A very luminous small cathode spot (10^{-8} to 10^{-4}m diameter) forms that passes **extremely high current densities (~ 10^8 to 10^{12} A/m^2).** This causes **erosion of the cathode by melting and vaporization** as well as **ejection of solid and molten particles**.

A schematic of a cathodic-arc deposition system is shown, where microscopic events at a cathode spot are also depicted. Particularly important in these systems is the **arc ignition mechanism**, sometimes a mechanical Striker but more often ignition by means of a break arc, and the means to confine the arc spot to the cathode surface.

To achieve **uniform film deposition the arc is steered magnetically**, which causes material to be eroded from the cathode in a series of flash evaporation events.

The metal ions and neutrals emitted are normally the desired species, whereas **microdroplets that manage to impinge on the substrate are a primary concern**. They arise from ablation of molten or solid cathode particles due to thermal shock



Ohring 2002

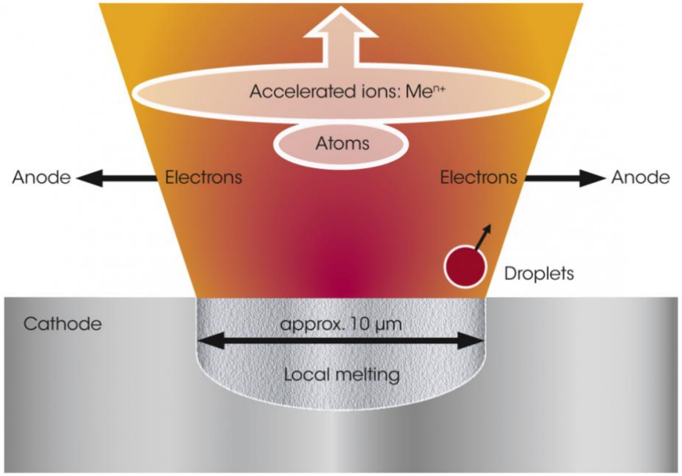
Cathodic arc plasma deposition

The medium which is the **primary current conductor is the ionised vapour** from one of the two electrodes.

Local melting spots with diameters in the range between a few tens of µm up to several hundred µm are formed.

These spots typically exist simultaneously at different locations on the surface of the cathode. **Atoms and ions are emitted together with droplets** of metal in a diameter range of a few hundred nm to a few tens of µm.

Due to the high local currents (power densities), **the majority of the vaporised material becomes ionised**, usually with a **degree of ionisation between 20 % up to nearly 100 %.** The ions often exhibit multiple ionisation and are accelerated to velocities between 10^4 m/s and 10^5 m/s during the evaporation process.



https://oerlikon-balzers.bibliothek-der-technik.de/

Cathodic arc plasma deposition

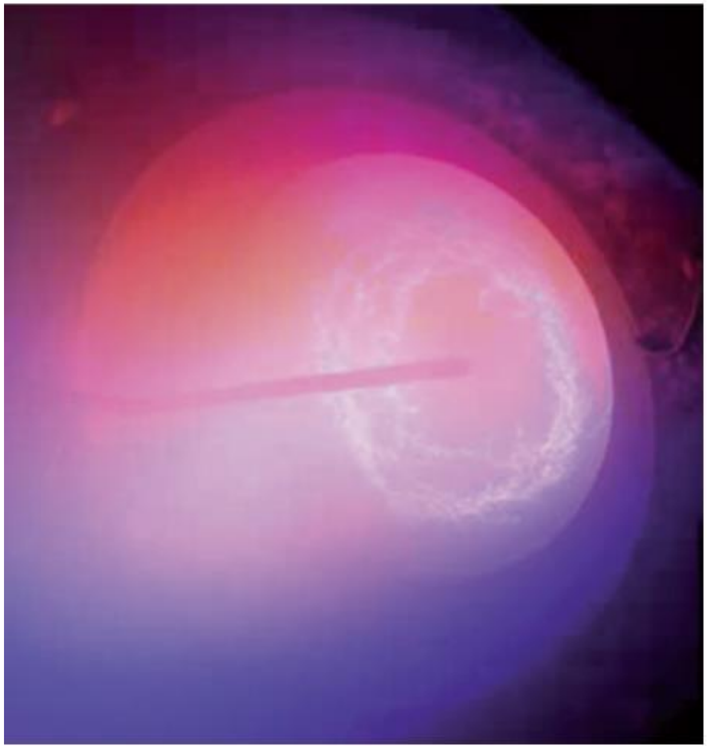
To cool the cathode, it is typically attached to a water-cooled evaporator body.

The arc is guided to the surface which is to be vaporised by means of suitable magnetic fields (magnetic flux density of typically 1 mT to 10 mT), which are generated using permanent magnets, electromagnets or a combination of these magnet types.

The image shows the arc track in a nitrogen atmosphere. The red glow is caused by the plasma excitation of the nitrogen. The medium which is the **primary current conductor is the ionised vapour** from one of the two electrodes.

The plasma exhibits a high concentration of ionised metal vapor with energies up to 100eV, which leads to dense and well adhering coatings.

For materials with high vapor pressure the ionisation degree is 5% and for those with low vapor pressure up to 100%. This leads to almost **stöchiometric compounds** through reaction with reactive gases.



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Cathodic arc plasma deposition

reactive gases are added at a controlled rate in a pressure range of 0.1 Pa to 10 Pa,

the round evaporators are flanged onto the wall of the chamber. Mechanical triggers generate the break arc for igniting the discharge.

several rows of evaporators allow for deposition of multilayer coating systems.

Using a row of evaporators with TiAl cathodes and an additional row of evaporators with TiSi cathodes, it is possible to create alternating TiAlN/TiSiN nanolaminates on rotating substrates.

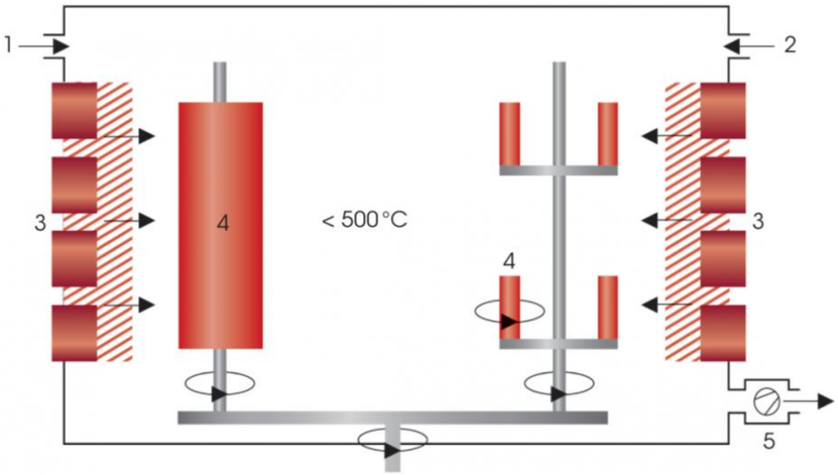

Fig. 11: Schematic layout of a coating chamber for cathodic vacuum arc evaporation

1 Argon
2 Reactive gas
3 Arc evaporator with coating material
4 Components
5 Vacuum pump

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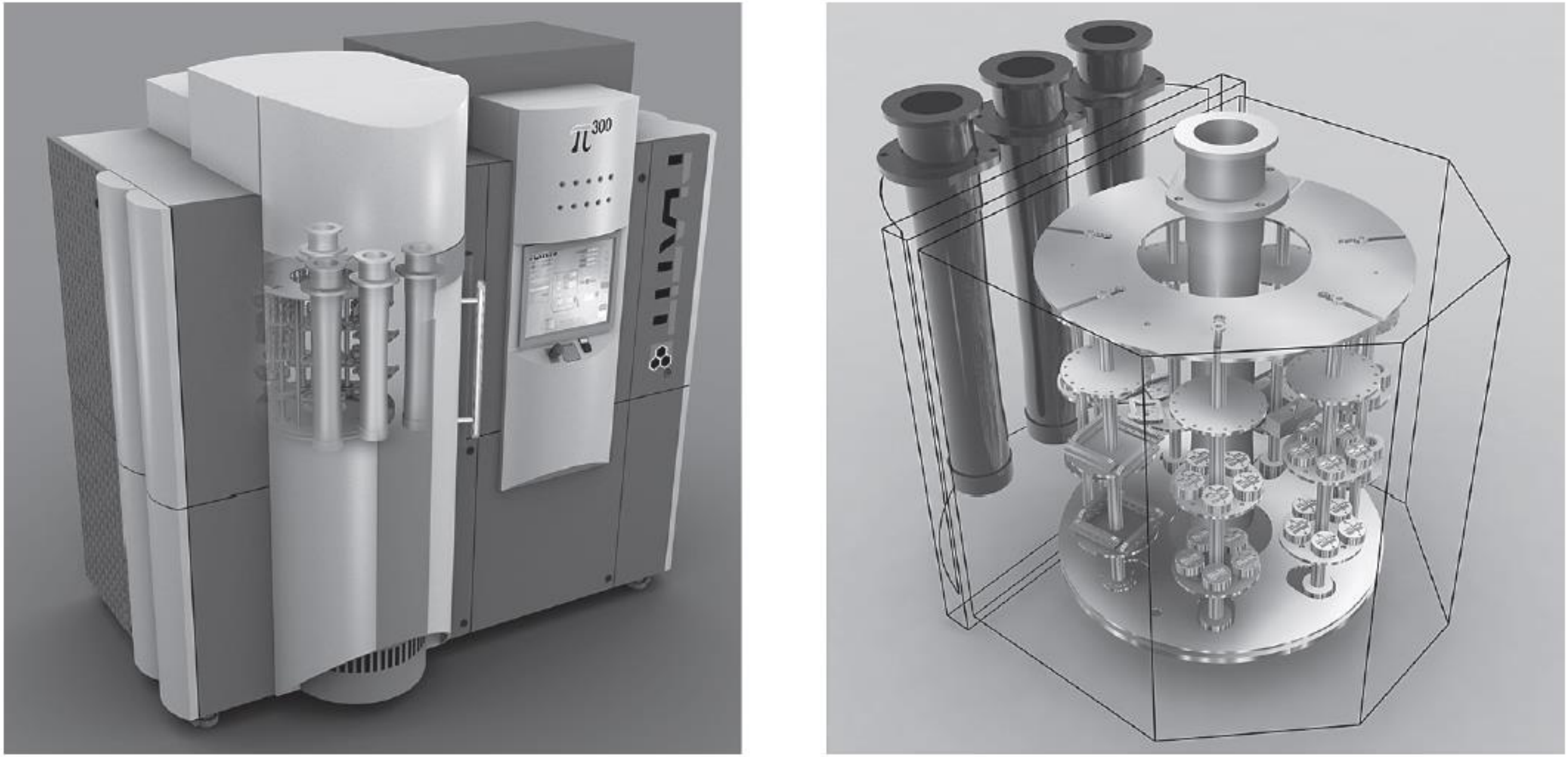
Cathodic arc plasma deposition – example from Platit AG



Blasek 2010

Cathodic arc plasma deposition

Cathodic arcs have been widely used in vacuum as well as reactive atmospheres to commercially deposit a large assortment of metal alloy and compound films.

In general **nitrides, carbides, oxides** and **mixtures** of these as well as **hard amorphous carbon coatings (DLC)** and **metal films** can be depositied.

The major application of refractory nitrides, carbonitrides, and carbides has been to wear- and abrasion-resistant **coatings in forming and cutting tools.**

Unlike CVD methods, the coatings are deposited at lower temperatures which **generally yield harder, finer grained deposits; furthermore, tool distortion is minimized**.

Interestingly, advantage is taken of the broad color range of **several binary and ternary nitrides in decorative coatings, e.g., for watch bands and eyeglass frames.**

Additionally, amorphous and diamond-like carbon films have been deposited in cathodic arcs, and optical coatings have been produced using anodic arcs.

Ohring 2002

high-power impulse magnetron sputtering (HiPIMS)

In the **magnetron modes of operation** described thus far, **the ionisation of the plasma lies significantly below that of cathodic vacuum arc evaporation** and the sputtered material in particular evidences a low degree of ionisation. In some cases, this has a negative effect on the coating properties.

In traditional magnetron sputtering processes for hard coatings, the **power density at the target is between 5 W/cm^2 and 30 W/cm^2**. To significantly increase the ionisation of the material, the power density at the target must be **increased by a factor of 10 to 100**. This can be accomplished using **high-power impulse magnetron sputtering** (HiPIMS).

In classic high-power impulse magnetron sputtering, power densities in the range **hundred W/cm^2 up to several thousand W/cm^2** are achieved temporarily.

A process of this nature **cannot be operated continuously** because otherwise the **target would overheat.**

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high-power impulse magnetron sputtering (HiPIMS)

Consequently, short pulse durations with a high pulse power are employed (even into the MW range).

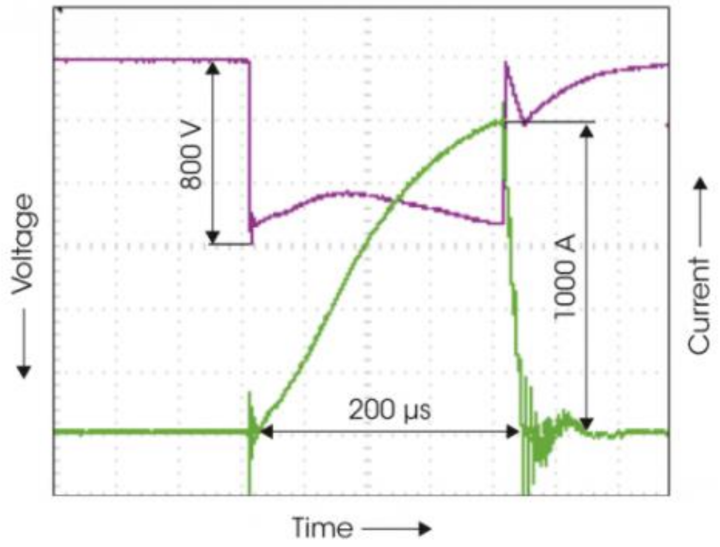
The pulse duration is usually in the range of 25 µs to 250 µs.

The pauses between two pulses are typically a few milliseconds long.

Often, frequencies of 10 Hz to 100 Hz are pulsed.

Depending on the target material and the pulse shape, the ionisation values of the sputtered material in the plasma can be several 10 % up to nearly 90 % of the values obtained with cathodic vacuum arc evaporation.

This makes the deposition of very dense coatings possible.



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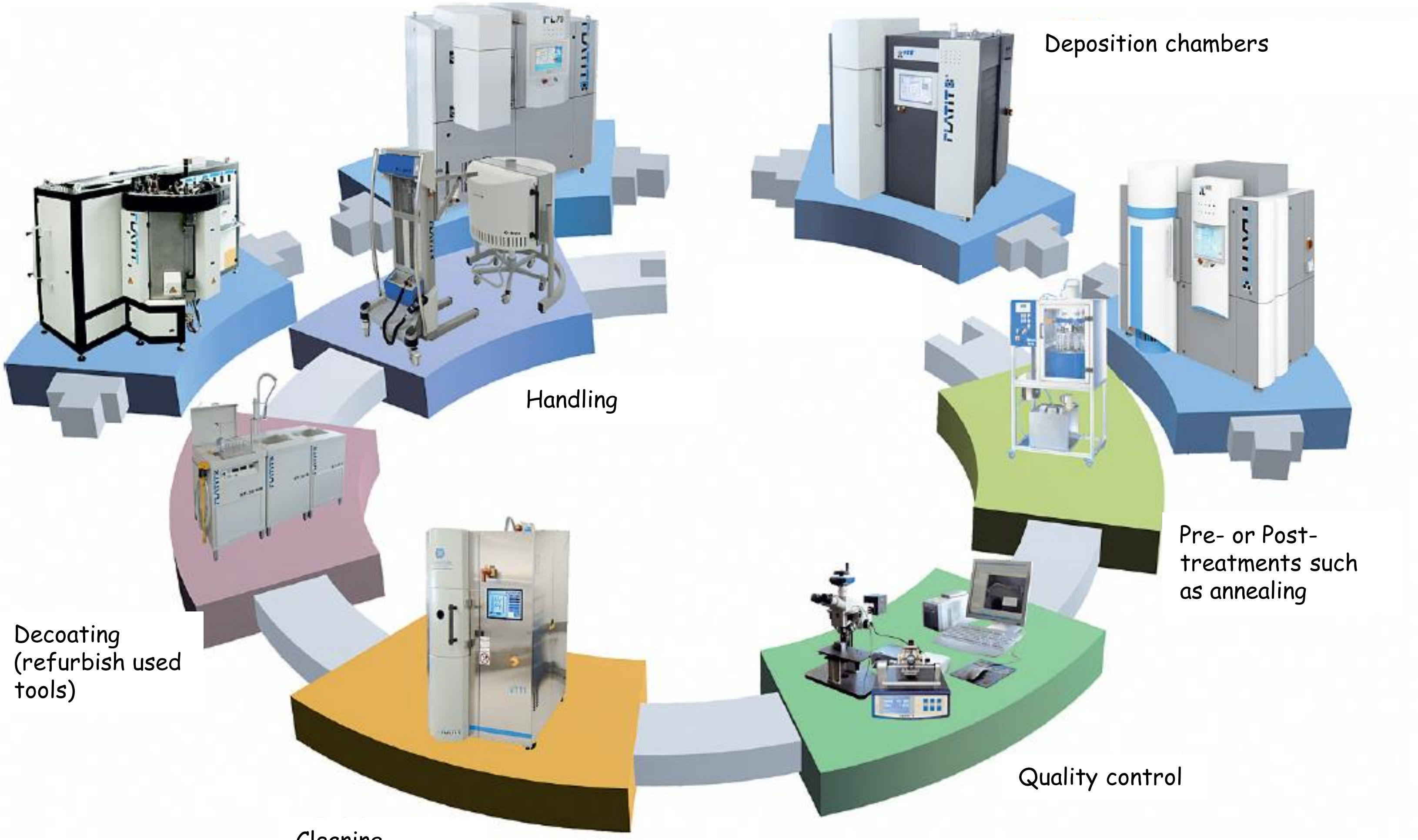
a coating centre (Platit AG)



Deposition chambers

Handling

Pre- or Post-treatments such as annealing

Decoating (refurbish used tools)

Quality control

Cleaning

Blasek 2010

summary I

- Interface crit. energy release rate vs residual stress
- Atomistic view: chemical bonding?, Kirkendall effects, interface mixing due to ion bombardment, mechanical locking
- Adhesion mechanisms, improvement: glue layer (oxide role), ion beam processing (energy!), polymers (plasma) activation of surface
- Measurement techniques adhesion: tear-off test (not quantitative), Rockwell adhesion, scratch techniques
- Nanoindentation: hardness under maximum load of 3-sided Berkovich tip. Young's modulus from linear unloading curve
- Thin film indentation: thin ice effect, 1/10 , fracture toughness difficult due to unknown crack path

summary II

- Definition hard coatings: hard 20-40GPa, superhard >40GPa, ~10 μm thick, intrinsically + extrinsically hardness contributions
- Applications: cutting tools, moulds, machine parts, medical & decorative
- Classifications: metallic: transition metal –N/C/B; covalent: c-BN, SiC, Diamond; ionic: Al/Si/Zr/Cr – O
- high intrinsic hardness: high binding energy, short interatomic distance, high degree of covalent bonding, high number of bonds per unit volume, modelling opportunity for search by DFT
- Desired properties: High (hot) H, K_c, $G_{adhesion}$, G_c between phases, low $\sigma_{res,}$ no reaction with substrate & environment, low friction coeff against material in application -> layered/gradient film to catch all properties & nanostructured for high extrinsic hardness
- Nitrides & Carbonitrides: "fcc TiN archetype", TiCN self-lubricating C layer, AlTiN and $Al_xCr_{1-x}N$: oxidation resistant -> oxides of Al & Cr, AlTiSiN forms superhard coating with AlTiN nanocrystals in a-SiN matrix
- Carbides: "fcc TiC archetype" with more covalent bond compared to TiN, TiC_xN_{1-x} better against C outdiffusion, TiCN nanocrystals in a-C:H matrix
- Borides: hexagonal TiB_2 with covalent B-B bonds, TiB2 nanocrystals in excess B-rich matrix, used for cutting of Al as Nitrides don't work
- Oxides: "hex Al_2O_3 archetype" but many polytypes, dominating for cutting tools (oxid resistance & hot hardness)
- Nanolayers: nanolaminates incl. epitaxial superlattices; toughening of nanolayers via crack deflection, ductile interlayers and interface delamination; superlattices with additional toughening with coherency strains, dislocation arrays at interfaces and oscillating Youngs Modulus (compared to single crystals)

summary III

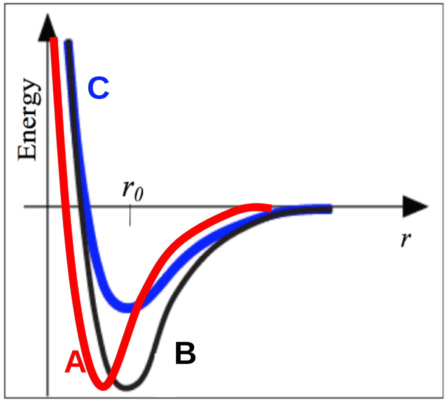
- Nanocomposites: strength due to grain refinement (Hall-Petch) and preventing GB sliding due to amorphous tissue phase at GB. Max hardness with 10nm grain size and 1-3nm tissue phase
- Arc plasma deposition: high I - low DC voltage, magnetically steered μm - sized spot with 10^{10} A/cm^2 leads to melting/evaporation/ejection of particles, ionization degree up to 100% leads to stöchimetric compounds in reactive arc deposition, ion energies up to 100eV leads to dense, well adhering films; samples (cutting tools etc.) on rotating planetary holder allows for nanolaminate deposition, all hard coatings possible but mostly used for forming and cutting tools as smaller grains compared to CVD as lower deposition T
- high-power impulse magnetron sputtering (HiPIMS): power densities on target like arc through 100μs pulses with 10-100Hz with almost 100% ionization degree and high energy ions leading to dense and well adhering coatings, but without particles as in arc deposition
- Coating process line includes handling, decoating, cleaning, QS, pre/post annealing and actual deposition equipment

questions

- What are thin film deposition strategies to improve thin film adhesion?
- You want to measure the Young's modulus of thin films. Explain the two rules of thumb related to the maximum indentation depth. Why is it important to stick to these rules?
- Why is a Berkovich tip used instead of a Vickers tip in nanoindentation?
- To calculate the contact area $A(h_c)$ from the contact depth h_c we do not assume a simple geometric relationship $A_c \sim h_c^2$. Explain why.

questions

- What are the different ways to classify hard coatings and how are they related to each other?
- Interatomic bonding determines the intrinsic hardness of a coating. How can it explain the difference between TiN vs. TiB2, and Diamond vs. Graphite?
- The figure below shows the interatomic potential of Material A, B and C. Rank them according to their expected intrinsic hardness and explain your choice. Which other factors, not visible in the interatomic potential are generally related to increased intrinsic hardness?



- Which considerations are crucial for material selection of a hard coating - substrate combination for a specific application?
- Discuss properties and microstructure of TiAlCSiN type coatings. Start with TiN and discuss the effect of adding other elements
- What is the effect of adding C to TiN in terms of properties and microstructure?

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questions

- Why is hexagonal TiB2 used for maching of Al and not TiN? Why are hardness values of TiB2 thin films above those of bulk material and which role does sputter deposition play in that hardening phenomena?
- Despite their relatively low intrinsic hardness, oxides are very frequently employed hard coatings. What are their main benefits? What are the main challenges during deposition of alumina?
- Explain most important hardening and toughening mechanisms of nanolayered coatings. What limits the minimum and maximum layer thickness and where is the hardness maximum located?
- Cathodoc arc deposition: What are the main advantages compared to conventional magnetron sputtering? What is meant by steered arc? State the challenges with arc evaporation deposition?
- How can magnetron sputtering achieve similar power densities on the target compared to arc deposition?
- Name the different steps in the workflow of an industrial deposition setting

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