Principles of Coating Technology

Part I - Basics

Part II – Deposition methods

6. Painting
7. Electro plating and anodic oxidation
8. Thermal Spraying
9. Build-up Welding
10. Vapor deposition (PVD / CVD)

8. Thermal Spraying
Thermal spraying

- Melting and acceleration of metallic or non-metallic material toward a substrate
- Surface normally is not molten
- Coating adhesion mainly results by mechanical clamping depending on surface roughness and adhesive processes

**Process sketch**

Formation of the coating structure

- Flowing and overlaying of molten particles
- Generation of oxides and pores
- Inhomogeneous coating structure
Application examples

- Steel layers for surface repair
- Ceramic thermal barrier coatings
- Corrosion protection of components
- Wear protection of components
- Hot gas corrosion protection (aircraft turbine blades)

Thermal spraying of a shaped part with a bronze layer
Thermal spraying of cylinder for the printing industry

Application examples

<table>
<thead>
<tr>
<th>Industry</th>
<th>Application areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive</td>
<td>Pistons, cylinders</td>
</tr>
<tr>
<td>Chemical industry</td>
<td>Valves, pumps, storage reservoir</td>
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<tr>
<td>Electrotechnical</td>
<td>Isolators, conductive layers, capacitor, fuel cells</td>
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<tr>
<td>Consumables</td>
<td>Electric irons, fry pan</td>
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<tr>
<td>Engineering</td>
<td>Compressors, pumps, cylinders,</td>
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<tr>
<td>Medicine</td>
<td>Coated implants</td>
</tr>
<tr>
<td>Aerospace industry</td>
<td>Run-in layer, thermal barrier coatings, blades,</td>
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<tr>
<td></td>
<td>combustion chamber,</td>
</tr>
<tr>
<td>Textile industry</td>
<td>Thread eye, thread brake</td>
</tr>
</tbody>
</table>
Surface pre-treatment

Pre-treatment absolute necessary for a sufficient coating adhesion

→ Removal of oils, lubricants, paints, oxides and scales

Pre-treatment methods:
• Removal of coarse contamination: grinding, turning, ...
• Degreasing of the substrate: dissolvent bath, steam cleaning, ultrasonic cleaning, ...
• Blast cleaning for an increased surface roughness (important: removal of blasting material)

Objective of pre-treatment: improvement of surface energy (surface activation)

Spray material

• Powder, rods, wires
• Hard metals and alloys
• Powder size 1 μm ... mm

Hard material

Metallic hard material

Carbide Nitride Boride
C, C, VC TaN ZrB

Non metallic hard material

Oxide Nitride Carbide
Al₂O₃ BeO Si₃N₄ SiC

Hard metal

Hard alloy

WC-Co WC-CoCr (W, Ti, Ta) Co-Cr

Metal

Cermet

Co₂Zr₂O₇ A1₂O₃
### Classification of thermal spay methods

#### Heat generation by combustion
- Flame spraying
- Detonation spraying
- High velocity oxygen fuel (HVOF)

#### by electrical heat generation
- Arc spraying
- Plasma spraying
- Laser spraying

#### Process temperature

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame spraying</td>
<td>3000 °C</td>
</tr>
<tr>
<td>Arc spraying</td>
<td>4000 °C</td>
</tr>
<tr>
<td>Plasma spraying</td>
<td>20000 °C</td>
</tr>
</tbody>
</table>

#### Particle velocity [1000 m/s]

#### Spray material

- **Molten bath spraying**
  - SnBi-alloys
  - Zn, Al, Cu, Ni, Cr, CrNi-rods, NiCr-alloys

- **Flame spraying**
  - Metals and metal alloys with melting point < 300 °C,
    partial thermoplastics
  - Zn, Al, Cu, Ni

- **Arc spraying**
  - Metals and metal alloys with melting point < 400 °C

- **Plasma spraying**
  - Metals, alloys, metal oxides, ceramics
  - Cu, Fe, Ni, Ta, W, Mo, Ti, Carbides, Borides, nitrides, silicides

#### Application areas

- Tool and model production
- Corrosion and wear protection, maintenance, tool production, thermal insulation

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**Principles of Coating Technology II**

GFE Schmalkalden e.V.
Molten bath spraying

- Simple process
- High variety of spray material
- Generation of compound coatings possible

Flame spraying: using flame as energy source

**Advantages:**
- Wide variety of spray materials
- Low equipment costs (<5000 EUR)
- Simple use
- Light spray gun
- Low radiation emission
- Low noise emission
- Coating of parts with any size possible

**Disadvantages:**
- Low coating strength
- High coating porosity
- Low deposition rates

**Modifications:**
- Wire flame spraying:
- Powder flame spraying

Wire flame spraying

powder flame spraying
**Wire flame spraying**

**Typical process parameters**
- Oxygen flow rate: 1.5 Nm$^3$/h
- Fuel flow rate: 1.2 Nm$^3$/h
- Compressed air consumption: 60 Nm$^3$/h, @ 4 – 6 bar
- Spray distance: 75 – 150 mm
- Deposition rate: 8 kg/h (Metalle)

**Spray materials**
- brittle materials (oxides, nitrides, borides and compound powders) as cored wire
- ductile materials as massive wire

**application**
- adhesion layers (NiAl, NiCr, Mo)
- corrosion protection (Zn, Al, ZnAl)
- wear protection (Mo)

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**powder flame spraying**

**Typical process parameters**
- Oxygen flow rate: 1.5 Nm$^3$/h
- Fuel flow rate: 1.2 Nm$^3$/h
- Spray distance: 75 – 150 mm
- Deposition rate: 2-6 kg/h (metals)
- Flame temperature: max. 3160°C ($C_2H_2 - O_2$)

- Powder material: metals, alloys, ceramics
- Powder grain size: $20 \mu m > d_{max} > 12 \mu m$
- Particle velocity: 50 m/s
- Substrate materials: metal, ceramics, wood, plastics, paper
Comparision of wire and powder flame spraying

Advantages of wire flame spraying:
- higher deposition rate
- Easier using of the spray material
- Higher coating strength
- Higher particle velocity
- Dense coatings
- Lower costs for spray material

Disadvantages of wire flame spraying:
- Higher equipment costs (<10000 EUR)
- Limited variety of spray materials
- High costs for ceramic materials
- High requirements on size accuracy (avoiding flame throwback)

High velocity oxygen fuel (HVOF)
- Flame spraying with higher particle velocity

Typical process parameters
- Flame temperature: min. 2500°C (kerosene – oxygen) max 3160°C (C_{2}H_{2} – oxygen)
- Flame velocity: 2000 m/s
- Oxygen flow rate: 15-55 Nm³/h
- Fuel flow rate: 3 Nm³/h C_{2}H_{2}, 40 Nm³/h (H_{2})
- Particle velocity: 650 m/s
- Deposition rate: 8 kg/h (metals); 4 kg/h (ceramics)
- Spray distance: 250 – 400 m

Applications
- Very dense and adherend hart metal / cermet coatings (WC-Co(Cr), Cr_{2}C_{3–Ni20Cr})
- Superconductive ceramic layers (YBa_{2}Cu_{3}O_{x})
- Adhesion layers (Ni20Cr, Ni5Al)
- Hot gas corrosion protection (MCrAlY)
Arc spraying

- Melting of two wire electrodes by an electrical arc
- Sputtering of the molten material with a gas jet (compressed air)

**Advantages:**
- high deposition rate
- No flammable gases
- Simple use
- Automation

**Typical process parameters:**
- Arc temperature: >4000 °C
- Arc power: 6 – 15 kW
- Particle velocity: max. 150 m/s
- Deposition rate: 20-40 kg/h
- Spray distance: 75 – 250 m

**Disadvantages:**
- Only electrical conductive wires

**Applications:**
- Corrosion protection
- Wear protection

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Plasma spraying

- Material will be molten by a plasma jet
- Plasma jets can be generated by an arc (nozzle with defined geometry)
- Plasma jets show a high gas velocity and high temperatures
- Plasma spraying can be used at atmosphere, in inert atmosphere, in water, in vacuum

**Typical process parameters (DC plasma spraying):**
- Jet temperature: >1000 °C
- Arc power: 6 – 15 kW
- Particle velocity: 50-500 m/s
- Deposition rate: 8 kg/h
- Spray distance: 60 – 140 m
### Plasma spraying

#### Applications
- Thermal barrier coatings (Y$_2$O$_3$-ZrO$_2$, CeO$_2$-ZrO$_2$)
- Wear protection coatings (Cr$_2$O$_3$, Al$_2$O$_3$-TiO$_2$)
- Corrosion protection coatings (Ni$_{20}$Cr, NiCrAl)

#### Advantages
- Every powder material with adequate difference of melting and evaporation temperature can be used
- Lower coating porosity
- Lower oxidation of spray material (vacuum plasma spraying: no oxidation)
- Reactive material can be used

#### Disadvantages
- High equipment costs (>100,000 EUR; vacuum plasma spraying <500,000 EUR)
- High deposition costs
- Ultraviolet radiation
- Noisy
- Limited component size

### Cold gas spraying

#### Typical process parameters:
- Gas temperature: < 600 °C
- max. particle velocity: 1000 m/s
- Max. deposition rate: 5 kg/h

#### Advantages:
- Avoiding of particle oxidation
- Extremely low coating porosity
- High coating adhesion on smooth substrates
- Low substrate temperature
Laser spraying

- Melting the particles with laser energy source

**Advantages**
- Low coating porosity
- Excellent coating adhesion due to metallurgical bonding
- Precise coating deposition on small components

**Disadvantages**
- Small alloying of coating and substrate
- High equipment costs (<400.000 EUR)

**Typical process parameters:**
- Particle velocity: <10 m/s
- Max. deposition rate: 2 kg/h

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Advantages and Disadvantages of thermal Spray processes

**Advantages**
- Wide variety of usable and available materials (metals, ceramics, oxides, …)
- Low heat input to the substrate
- High deposition rates
- Wide Range of coating thickness (50 μm - 5 mm)

**Disadvantages**
- Low adhesion strength due to a lower metallurgical bonding (damageable by impacts, coating delamination)
- High porosity of the coatings (reduced corrosion resistance)
- For dense coatings post treatment necessary (shot peening, re-melting, …)
- Metallurgical modification of the spray material due to the process conditions
- Limitations of coating accuracy (edges, radius, …)
Advantages and Disadvantages of thermal Spray processes

Problematic coatings on edges

Different coating thickness due different impact angles of the sprayed particles

9. Build-up welding
Build-up welding

- Generation of a connection between a metallic substrate and the plating material
- Deposition welding occurs if the joining partners are remelted and alloyed in the interface area
- Deposition welding is possible if both materials (substrate and weld metal) are suitable for welding (mixing without formation of intermetallic phases is possible)

Example: gas build up welding

For generation of coatings energy input is necessary
- for surface activation is not possible
- To partial or fully melt the substrate and the weld material
- To alloying within the contact area

Energy input by
- Heating (thermal activation)
- Radiation
- Elastic-plastic deformation (mechanical activation)

All welding methods can be used for build-up welding
Best methods are welding methods with
- high deposition rates
- low dilution between substrate and weld material
## Build-up welding

### Deposition by welding

| Hard-facing: | generating of high wear resistant coatings |
| Plating: | generating corrosion resistant coatings |
| Buffering: | joining two dissimilar materials |

### Advantages of deposition welding

- All components can be welded
- Good coating adhesion
- Pore free coatings
- Good heat conduction into the component

### Weld materials

#### Weld materials (hard-facing)

- Iron hard alloys (Fe-Cr-C + W, V, Nb, Mo, Ti, B, Mn, Si)
- Nickel hard alloys (Ni-B + Cr, C, Si, WSC)
- Cobalt hard alloys (Co-Cr-W-C + Mo, V, Nb)

#### Weld materials (plating)

- Stainless steels (Fe-Cr-Ni + Mo, Al)
- Nickel based alloys (Ni-Cr + Al, Mo, W, Nb, Ti, Fe)

#### Weld materials

- Wire electrodes (cored, massive)
- Strip electrode (cored, massive, alloyed)
- Powder (molten, agglomerated, mechanical alloyed)
Weld material: fused tungsten carbide (WSC)

- Optimized fine microstructure of the build-up weld possible (can be generated by a C-content between 3.9 and 4.2 mass %, reduced contamination, fast cooling)
- Fine grained WSC show hardness > 2000 HV and a good ductility
- Faster dilution of WSC with coarse grains, crack formation at dynamical load possible
- Reinforce of metallic matrix with WSC-particles lead to strengthening
  - Higher hardness up to >3000 HV
  - Increased abrasion resistance

Dilution during build up welding

- Melting of the substrate for a metallurgical bonding
- Dilution by mixing of substrate and weld material
- Determination of the degree of dilution by proportion of the composition of surface material and weld material

- Modification of surface composition by dilution
- reducing the degree of dilution by multilayer welding
- Setting a defined build-up weld composition by selective alloying of the dilution

Degree of dilution [%] \( A = \frac{A_e}{A_e + A_s} \times 100 \)
Requirements for the build-up welding

- Low dilution
- Homogenous microstructure
- Homogeneous weld penetration
- Low roughness
- Uniform coating thickness
- Homogenous coating composition
- Preferable smooth surface
- Without penetration cuts

Criteria for the build-up weld material

- Operational demands
- Weldability
- Availability
- Metallurgical interaction between substrate and welding material
- Heat treatment
- Dilution sensibility
- Resulting requirements on the welding method

Heat treatment /pre treatment

- Heat treatment before welding to reduce thermal stresses
- Slow cooling after welding to reduce thermal stresses
- Regarding dispersion kinetics to avoid unwanted mechanical and corrosive properties and phases

Criteria for the build-up weld method

- Process stability
- Availability
- Coating quality (dilution, thickness, roughness)
- Post treatment possibilities
- Component geometry
- Cost effectiveness

Quality of build-up welded coatings

Welding defects: pores and non diluted particles

Ideal welding:

- Low dilution
- Small heat affected zone
- Homogeneous carbide distribution
Build-up welding

Methods for build-up welding

- Fusion welding
  - Induction welding
  - Friction welding
  - Roll seam welding
- Pressure welding
- Gas welding
- Arc welding
- Beam welding
- Resistance welding
  - Laser beam welding
  - Electron beam welding
- Manual arc welding
- Gas shielded arc welding
- Submerged arc welding
  - Consumable electrode
  - Metal shielding gas welding
  - Non-Consumable electrode
  - Plasma welding
  - Tungsten shielding gas welding

Gas welding

Process characteristics
- Low melting efficiency
- Pre-heating necessary
- Low cost equipment
- Flexible using
- Inefficient process, useful only for repair

Plough blade for agriculture
Roll mill for aluminum production
Build-up welding

Process characteristics
- Energy input by an electrical arc
- Arc between electrode and substrate
- Arc and melt bath can be protected by shielding gas (Ar, He)
- Feeding of weld material by electroless wire or rod

Important process parameters
- Using of DC with positive polarity of the substrate
- Control of polarity and current by power generator
- Ignition of the arc manually or automatically

Important process parameters
- Weld parameter (polarity, current control,...)
- Arc contour
- Composition of weld material
- Processing gas (composition, pressure)

Tools for sand exploitation
Boring tools for oil exploitation
Bucket digger in mining industry
**Important processes**

- For ignition of an arc free charge carriers necessary
- Ionization of gases between electrodes by high electrical field strength
- Heating of the cathode by ions lead to electron emission
- Partially ionized gas (thermal plasma) within the arc
- Transport of charge carriers lead to magnetic field and to constriction of the arc (cathode spot)
- Resulting forces and effect influences contour and temperature of the arc and melting of material

**Forces during arc welding**

- Wire electrode
- Electromagnetic force (Pinch-Effect)
- Surface tension
- Drag forces by plasma flow
- Electrostatic forces
- Repulsion power of evaporation material

**Influence of plasma gas flow**

- High energy density at the electrode tip → compression of the magnetic field (Pinch Effect)
- Expansion of hot gases at the electrode tip → assist of material flow
- Gravitational force influences gas and material flow

**Pinch Effect**

- Strength of magnetic field in a live wire is proportional to local current density
- Reduce of cross section at the liquid electrode tip increases current density → Strong magnetic field, line out of the molten particle

**Viscosity and surface tension**

- Influencing size of formed material droplets
- Depending on composition, gas absorption (oxygen absorption reduces surface tension) and temperature
- Low surface tension and viscosity lead to smaller droplets
Build-up welding

**Arc welding – control of current voltage characteristics**

- **External current control - ΔU control**
  - Power generator with dropping characteristics
  - Voltage will be used for wire feeding
  - Shortening the arc length reduces voltage drop
    - reduced wire feed rate
    - increased arc length

- **Internal current control - ΔI control**
  - Nearly constant voltage
  - Shortening the arc length increases welding current
    - increased melt of electrode
    - increased arc length
    - control

**Manual arc welding**

- Using manual guided rod electrodes
- Arc ignition by a shortcut of the electrode with the component surface
- Only power generators with dropping characteristics (due short cut ignition)
- Arc is firing between component end electrode
- Dilution of droplets with molten component surface
**Submerged arc welding**

- Arc is in a cavern covered from a partially molten material
- Cavern will be stabilized by gas pressure within
- Liquid powder material solidifies on the weld bead surface

**Characteristics**

- Welding current <5000A
- High melting and deposition rate
- High dilution necessary for metallurgical bonding
- Magnetic guiding of the arc for a uniform melting
- Often three-coat deposition due to the high dilution

**Shielding gas welding**

- Arc, material transfer and welding bath arc protected by an external gas flow
- Specified reactive material and large melt baths are protected by protection caverns, showers or addition shielding gases
- For a uniform heat transfer and uniform penetration, welding system is oscillating
- Kinematic of the oscillation influences coating structure and coating surface

**Process of shielding gas welding**

- Melting of used electrode
- Partial melting of substrate
- Using of inert (metal shielding gas welding MIG, tungsten shielding gas welding WIG) or active gases (metal active gas welding MAG)

**Characteristic:**

- Welding current 25 - 650 A
- Welding gases Ar, He, N₂ (shielding gases) CO₂, O₂ (active gases)
- High heat input, low deposition rate
- Simple configuration with easily automation
- for uniform heat input optimized arc guiding necessary
**Build-up welding**

**tungsten shielding gas welding**

- Arc is firing between non melting electrode (tungsten) and component
- Arc and melt bath are protected by a shielding gas (Ar, He)
- Additional transfer of the welding material by wire or rod
- Using DC with positive polarity of the substrate
- Al and Mg material: negative polarity due oxide layer → high thermal load or AC mode

**Characteristic:**
- Good weld bead quality (roughness, homogeneity, porosity)
- High flexibility of usable material (reactive metals)
- Control of dilution, penetration cut depth and substrate pre-cleaning by power supply
- Good automation
- Low melting and deposition rates (cost efficient only for small areas)

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**Electro slag welding**

- Melting of welding material by resistive heating
- Liquid slag of the weld powder with high resistivity is used for heat generation
- Avoiding short cuts and arc re-ignition by moderate resistivities

**characteristics**
- Welding current max 3000 A
- High melting rate
- High process stability
- Small uniform penetration cut
- Often two-coat deposition for higher corrosion resistivity
Plasma welding

- Heat source: plasma jet between non-melting electrodes
- Two separate arcs: between plasma electrode and plasma jet (pilot arc, plasma generation) between plasma electrode and substrate surface (melting substrate)

Advantages
- High automation
- High melting and deposition rate
- High process flexibility
- High material flexibility (power injection by a gas jet)
- Powder material (composition, density, shape, ...) influences welding process

Laser build-up welding

Advantages of the laser beam
- Exact controlled and local heat source
- High energy density
- Coating thickness 0.1 – 1.5 mm

Disadvantages of conventional laser processes
- Weld material powder: High powder losses, low deposition rates
- Weld material cold wires: low deposition rate and high dilution

→ Improved performance by using hot wires possible
## Comparison of different build-up welding methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Electrode</th>
<th>Submerged</th>
<th>WIG</th>
<th>MIG/MAG</th>
<th>Electro-deposied</th>
<th>Open-Arc</th>
<th>Autogen</th>
<th>Gas-powder</th>
<th>Plasma (PTA)</th>
<th>Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal deposition rate (kg/h)</td>
<td>3</td>
<td>10:20</td>
<td>2</td>
<td>10</td>
<td>15</td>
<td>10</td>
<td>1</td>
<td>5</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>Dilution (%)</td>
<td>15-25</td>
<td>10-30</td>
<td>5-10</td>
<td>20-30</td>
<td>10-15</td>
<td>10-35</td>
<td>1-5</td>
<td>&lt;0,5</td>
<td>5-15</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Weld velocity</td>
<td>medium</td>
<td>medium</td>
<td>slow</td>
<td>fast</td>
<td>medium</td>
<td>fast</td>
<td>slow</td>
<td>medium</td>
<td>&gt;medium</td>
<td>fast</td>
</tr>
<tr>
<td>Weld material - shape electrode</td>
<td>Wire, band</td>
<td>Rod, wire</td>
<td>Wire, band</td>
<td>Wire, band</td>
<td>Rod, wire</td>
<td>Powder, powder</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weld material - size or Ø (mm)</td>
<td>2.8-8</td>
<td>0.8-5 100 (*)</td>
<td>0.6-5</td>
<td>0.6-4.8 100 (*)</td>
<td>0.3-0.8 100 (*)</td>
<td>1-2.8</td>
<td>0.6-4</td>
<td>Powder size &lt; 250 µm</td>
<td>Powder size &lt; 250 µm</td>
<td>&lt;0.6 mm</td>
</tr>
<tr>
<td>Thermal input</td>
<td>high</td>
<td>high</td>
<td>low</td>
<td>medium</td>
<td>high</td>
<td>high</td>
<td>high</td>
<td>medium</td>
<td>&lt;medium</td>
<td>low</td>
</tr>
<tr>
<td>Normal coating thickness (mm)</td>
<td>2-10</td>
<td>5-10</td>
<td>1-3</td>
<td>2-10</td>
<td>10-30</td>
<td>5-10</td>
<td>1-5</td>
<td>1-3</td>
<td>2-10</td>
<td>1-2</td>
</tr>
</tbody>
</table>

*) using band with Bandwith up to ~100 mm

## Advantages
- Wide variety of coating thickness (µm to mm)
- Wide variety of weldable materials
- Metallurgical bonding to the substrate
- High coating adhesions
- Dense coatings

## Disadvantages
- Only metallic substrates
- Thermal influencing of the substrate
- Variation of coating composition by dilution of the substrate material
10. Vapor deposition (PVD / CVD)

Different vapour deposition methods are possible

<table>
<thead>
<tr>
<th></th>
<th>Physical vapor deposition</th>
<th>Chemical vapor deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>evaporation</td>
<td>sputtering</td>
</tr>
<tr>
<td>Gas Pressure</td>
<td>10 Pa</td>
<td>1 Pa</td>
</tr>
<tr>
<td>temperature</td>
<td>150 -500 °C</td>
<td>150 -500 °C</td>
</tr>
<tr>
<td>Coating Thickness</td>
<td>0,1 – 2 μm</td>
<td>0,1 – 2 μm</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>0,01 μm/min</td>
<td>0,01 μm/min</td>
</tr>
<tr>
<td>remarks</td>
<td>Better adhesion compared to evaporation</td>
<td>Better adhesion compared to sputtering good control possibility</td>
</tr>
</tbody>
</table>
Application examples

- **Hardness:** TiN coated cutting tools
- **Wear resistance:** CrN coated forming tools
- **Corrosion resistance:** Nitro-carburisation
- **Conductivity:** Gold coats for electronic parts
- **Optical:** Heat insulation layers
- **Metallization of plastics:** Cu, Al, Sn, Ag, Mg, ...
- **Bio compatibility:** For medicine parts
- **Decoration:** Coloured parts

Materials and coating systems

- Borides, carbides, nitrides and oxides
- Multi component systems of the elements
- Different structures possible (amorphous, tetragonal, cubic, diamond, ...)

Pre-treatment

- Mechanical cleaning (blasting)
- Degreasing
- Etching
- Surface activation
**PVD (Physical Vapor Deposition)**

**Procedure:**
- Generation of evaporated phase
- Transfer of vaporized particles
- Deposition of the particles on the substrate (nucleation)
- Coating formation
- Ceramic coatings are built from metallic component and reactive gas
- For better coating adhesion a negative potential of the substrate is possible (acceleration of ions)

**Characteristics:**
- Vacuum process
- Deposition temperature < 600°C
- Reactive processes possible

**Process modifications:**
- Evaporation (vapour generation by evaporation)
- Sputtering (sputtering with ions)
- Ion plating (particle deposition into substrate)

**Modification of the coating structure by**
- Thermal energy
- Energy of ions and neutrals within the process gas
- Bonding energy of the materials (substrate, ions, atoms, coating material)
- Surface activation energy
### PVD (Physical Vapor Deposition)

**Advantages:**
- Coating properties are the result of target composition (compounds of carbides or nitrides)
- Metallic ceramics show very high hardness
- PVD coatings are normally chemical inert (reduced adhesion wear)
- High thermal stability (coating decomposition with oxides at temperatures >400°C)
- Thin and form fitting coatings (sharp edges)

**Disadvantages:**
- Deposition in the line of sight (high effort for work piece positioning)
- No possibility to deposit coating in holes and slots
- Process needs high vacuum (high costs, work pieces must be vacuum qualified)
- Metallic pre cleaned surfaces necessary (for good adhesion)
- No corrosion protection with PVD coatings (porous structure)

### Coating structure:
- Coating structure depends on substrate temperature, pressure an coating material
- Different models can be used to predict expected coating structure

<table>
<thead>
<tr>
<th>Zone 1</th>
<th>Needle shaped crystallites, porous structure by shadowing effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 2</td>
<td>Columnar structure column diameter is increased with temperature</td>
</tr>
<tr>
<td>Zone 3</td>
<td>Recrystallized dense structure, grain growth depend on diffusion effects</td>
</tr>
<tr>
<td>Zone T</td>
<td>Transition region with fibrous structure, diffusion compensate shadowing</td>
</tr>
</tbody>
</table>

Modell von Movchan und Demchisnik in high vacuum for the materials Ti, Ni, W, ZrO₂, Al₂O₃

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Principles of Coating Technology II
PVD typical coating systems

<table>
<thead>
<tr>
<th>Coating system</th>
<th>TiN</th>
<th>TiCN</th>
<th>TiAlN</th>
<th>CrN</th>
<th>ZrO₂</th>
<th>Al₂O₃</th>
<th>WC/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro hardness</td>
<td>HV 0,05</td>
<td>2300</td>
<td>3000</td>
<td>3500</td>
<td>1750</td>
<td>1200</td>
<td>3500</td>
</tr>
<tr>
<td>Friction coefficient</td>
<td>0,4</td>
<td>0,4</td>
<td>0,5</td>
<td>0,6</td>
<td>k.A.</td>
<td>&lt;0,2</td>
<td></td>
</tr>
<tr>
<td>Heat conductivity</td>
<td>W m⁻¹K⁻¹</td>
<td>70</td>
<td>100</td>
<td>50</td>
<td>12</td>
<td>0,7 - 2,4</td>
<td>25</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>10⁻⁶ K⁻¹</td>
<td>9,4</td>
<td>9,4</td>
<td>7,5</td>
<td>9,4</td>
<td>7,5 - 10,5</td>
<td>7,2 - 8,6</td>
</tr>
<tr>
<td>Max. working temperature °C</td>
<td>550</td>
<td>400</td>
<td>800</td>
<td>700</td>
<td>700</td>
<td>1750</td>
<td>300</td>
</tr>
</tbody>
</table>

PVD - Evaporation

Characteristics:
- Heating and evaporation of coating material within a heat source
- Condensation of vapour on the cold substrate
- Heating possible by inductive heating electron beam, arc evaporator

Advantages:
- High deposition rates
- Uniform coatings
- Low temperatures of the substrate

Disadvantages:
- Reduced coating adhesion
- Only for components with simple geometries
Vapor deposition (PVD)

**PVD - sputtering**

**Characteristics:**
- Generation of a high energetic vacuum plasma by high voltage
- Sputtering of a target of coating material by ions of the plasma
- Sputtered material is condensed on the substrate

**Advantages:**
- Good coating adhesion
- Non conductive coatings possible

**Disadvantages:**
- Non uniform coating thickness distribution
- Only for components with simple geometries

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**PVD – ion plating**

**Characteristics:**
- Combination of evaporation and sputtering
- Evaporation of coating material
- Plasma generation by glow or arc discharge
- Ionisation of evaporated material by the discharge
- Acceleration of ionised components to the substrate by an electrical field
- Chemical reactions within the discharge and on the work piece surface

**Advantages:**
- Uniform and dense coatings
- Good coating adhesion
- Moderate deposition temperatures (250-450°C)
CVD – chemical vapor deposition

Characteristics:
- Precursor material in a slightly volatile bonding
- Heating and evaporation of precursors
- Transfer to the reaction chamber (vacuum or normal pressure)
- Thermal or plasma assisted chemical reaction
- Deposition of reaction products on the surface

Advantages and disadvantages:
- Uniform coatings
- Deposition of complex parts possible
- High deposition temperatures (300-1200°C)

Chemical Reactions for metallic materials:
- CH₃SiCl₃ → SiC + 3 HCl (1200°C)
- TiCl₄ + ½ N₂ + CH₄ → Ti(C,N) + 4 HCl (1000°C)
- BCl₃ + NH₃ → BN + 3 HCl (500 – 1500 °C)
- Al₂C₆ + 3 CO₂ + 3 H₂ → Al₂O₃ + 3 CO + 6 HCl (800 – 1400 °C)
### Principles of Coating Technology II

#### Vapor deposition (CVD)

**CVD – chemical vapor deposition**

**Process temperatures**
- High temperature CVD (> 1000°C)
- Middle temperature CVD (700 - 850°C)
- Low temperature CVD (< 500°C) (Plasma enhanced CVD)

**substrates:**
- Hart metals,
- Temperature stable steels

**applications:**
- Hard coatings for forming and cutting tools
- Wear resistant coating
- Reduction of cutting forces and process temperatures

**Plasma CVD processes**

**Characteristics**
- Reaction energy provided by an glow discharge or a plasma
- Reducing of deposition temperature (500 °C down to 100°C possible!)
- Chemical reaction in the discharge boundary near the substrate
- Plasma excitation by: DC, pulsed DC, high frequency
- Substrate heating: Ion bombardment, separate heater

**Advantages**
- Lower deposition temperature
  - low influence to the substrate, temperature sensitive materials can be used
- Uniform coating surface
- Using of plasma-polymerisation possible
  - Deposition of cross-linked molecule and structures
  - Deposition of Diamond coatings and diamond like carbon (DLC) coatings

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Mitsubishi Materials

TiN coated inserts
Possible advantages of carbon based coatings

- Combination of different properties in one coating system
- High hardness
- Low friction coefficient
- Chemical inert again acids
- Higher thermal conductivity
- Low thermal expansion coefficient
- Electrical insulation
- Transparency
- Smooth surface

- Reduced adhesion on shaped parts (injection moulding)
- Windows for high power laser systems
- DLC coated rank shaft
**Vapor deposition (CVD)**

CVD – hardness of different coating systems

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamant</td>
<td>10000</td>
</tr>
<tr>
<td>ta-C</td>
<td>8000</td>
</tr>
<tr>
<td>a-C:H</td>
<td>6000</td>
</tr>
<tr>
<td>a-C:F</td>
<td>4000</td>
</tr>
<tr>
<td>a-C:H:F</td>
<td>2000</td>
</tr>
<tr>
<td>TiN</td>
<td>1000</td>
</tr>
<tr>
<td>TiB</td>
<td>800</td>
</tr>
<tr>
<td>TiB₂</td>
<td>600</td>
</tr>
<tr>
<td>TiC</td>
<td>400</td>
</tr>
<tr>
<td>TiB₂N</td>
<td>200</td>
</tr>
<tr>
<td>TiAlN</td>
<td>100</td>
</tr>
<tr>
<td>TiAlN₂</td>
<td>80</td>
</tr>
<tr>
<td>TiB₂N₂</td>
<td>60</td>
</tr>
<tr>
<td>TiB₂N₂₂</td>
<td>40</td>
</tr>
<tr>
<td>TiB₂N₂₂₂</td>
<td>20</td>
</tr>
<tr>
<td>TiB₂N₂₂₂₂</td>
<td>10</td>
</tr>
<tr>
<td>TiB₂N₂₂₂₂₂</td>
<td>8</td>
</tr>
<tr>
<td>TiB₂N₂₂₂₂₂₂</td>
<td>6</td>
</tr>
<tr>
<td>TiB₂N₂₂₂₂₂₂₂</td>
<td>4</td>
</tr>
<tr>
<td>TiB₂N₂₂₂₂₂₂₂₂</td>
<td>2</td>
</tr>
<tr>
<td>TiB₂N₂₂₂₂₂₂₂₂₂</td>
<td>1</td>
</tr>
</tbody>
</table>

**Tetrahedral structure of diamond**

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**Vapor deposition (PVD / CVD)**

### Advantages

- Very thin layers possible
- High variety of usable materials and substrates
- High variety of coating structures and modification (graded, multilayer, diamond like,...)
- Very high coating hardness possible
- Dense coatings

### Disadvantages

- high pre treatment effort
- Reduced adhesion at local high loads (eggshell-effect)
- CVD: very high temperatures, influence on the substrate
- PVD: limitations of coating complex geometries with holes and slots
Thank you for your attention
Part II