Ceramic Coating

Thermal spray, CVD and PVD
Outline:

- Materials, applications
- Processing
- Factors
- Thermal spray
- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD)
Properties of ceramic films and coating

- High hardness
- Inertness
- Corrosion, oxidation and wear resistance
- Electronic and optical properties
Application of ceramic coating

- Aircraft-engines
- Fan blades
- Metal cutting tools
- Racing cars, Automobile manufacturers
- Diesel engines (piston dome and exhaust)
- Land-based turbines and marine engines
- Carbon-carbon composites
- Heat exchangers
- Wear resistant products
- Aerospaces
- Medical implants
- Electronic and optical devices: wave guides, detectors
Simple materials

- ** Metals:**
  - Al, gold, tungsten, nickel, chromium, platinum

- ** Nitrides and Carbides:**
  - SiC, SiN, TiN

- ** Insulating and protective coatings:**
  - SiO$_2$, ZrO$_2$

- ** Optical coatings:**
  - MgF$_2$, ZnS, ZrO$_2$
Complex oxides

- Electronic insulators: $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{Ta}_2\text{O}_5$
- Ionic insulators: $\text{ZrO}_2$, $\text{CeO}_2$
- Electron conductors: $\text{RuO}_2$, $\text{ReO}_2$, $\text{IrO}_2$
- Transparent conductors: $\text{SnO}_2$, Indium tin oxide
- Non-stoichiometric compounds: $\text{La}_{1-x}\text{Sr}_x\text{VO}_3-x/2$
- Superconducting oxides: $\text{YBa}_2\text{Cu}_3\text{O}_7$
- Ferroelectrics: $\text{PbTiO}_3$-$\text{PbZrO}_3$, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$
Surface coating techniques

- Traditional enamels: glass-based coatings of inorganic composition applied in one or more layers to protect steel, casting iron or aluminium surfaces
- Chemical coatings: electroplating of metals such as copper and nickel
Surface coating techniques

- Sol-gel coatings: the pyrolysis of organometallic precursors such as metal alkoxides
- CVD: vapor phase transport to grow epitaxial and highly structured thin film including insulating oxide films on single crystal silicon substrate
- PVD: evaporation, sputtering, laser ablation and iron bombardment
Evaporation

- Materials $\rightarrow$ melted and vaporized by heated tungsten/molybdenum boat/electron beam $\rightarrow$ deposited on substrate
- For metal, alloys and stable compounds such as silica, yattria
Sputtering

การเกิดการสะสมของวัสดุ โดยละเอียดที่แยกออกมาจาก target หลุดออกมาโดยการชนของอิออนที่มีพลังงานสูง เช่น gas plasma หรือ excited ion beam จากนั้นจะค่อยๆ ของวัสดุจะมาจากสะสมบนผิว substrate
Thermal spray

- ผังชาร์มิกทรีฟองโลหะถูกกล่อมและพ่นผ่านบริเวณที่มีอุณหภูมิสูง ที่สระว่างตัวกระแทกฟ้า โดยเป็น Gas plasma และ/หรือ Combustion gas flame
  - Flame spraying
  - Plasma spraying
Thermal spray processes
Flame spraying

- Powder feed (wire) of coating material is fed through an oxy-fuel gas—ex. \( \text{C}_2\text{H}_2 \) or \( \text{C}_3\text{H}_8 \) flame
- \( \text{ZrO}_2 + \text{Al}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{ZrO}_2 \)
Wire spray coating

Specifications:
- Coating Material Form: Wire
- Heat Source: Oxy-Fuel Combustion
- Flame Temperature (in °C): 3000
- Gas Velocity (m/sec): Up to 300
- Porosity: 10 to 15%
- Coating Adhesion (MPA): 14 to 20

Figure from Plasmatron
Powder flame spraying

Specifications:
- Coating Material Form: Powder
- Heat Source: Oxy-Fuel Combustion
- Flame Temperature (in °C): 3000
- Gas Velocity (m/sec): Up to 300
- Porosity: 10 to 15 %
- Coating Adhesion (MPA): 14 to 20

Figure from Plasmatron
Wire Arc spray coating

Specifications:
- Coating Material Form: Wire
- Heat Source: Electric Arc
- Flame Temperature (in °C): 3600
- Gas Velocity (m/sec): Up to 300
- Porosity: 10 to 15 %
- Coating Adhesion (MPA): 28 to 40

Figure from Plasmatron
Plasma spraying

- Thickness > 50µm
- Substrate: metal alloy, ceramics

Applications:
- Wear/erosion and corrosion resistance
- Thermal barriers
- Electrical and magnetic
- Aircraft
What is Plasma?

- A gaseous collection of electrons, ions and neutral molecules

- Plasma gun:
  - Cathode (-)
  - Anode (+) with water cooling
  - Inert gas (Ar, N₂)
  - Powder feeder
  - Nozzle (+)
Air plasma coating

Specifications:

- Coating Material Form: Powder
- Heat Source: Plasma Flame
- Flame Temperature (in °C): 12000 to 20000
- Gas Velocity (m/sec): 500
- Porosity: 2 to 10 %
- Coating Adhesion (MPA): 40 to 70

Figure from Plasmatron
High velocity Oxy-fuel (HVOF)

Specifications:
- Coating Material Form: Powder
- Heat Source: Oxy-Fuel Combustion
- Flame Temperature (in °C): 1500 +
- Gas Velocity (m/sec): 1500 +
- Porosity: 1 to 5 %
- Coating Adhesion (MPA): 70 +

Figure from Plasmatron
Detonation gun (D-gun)

- D-gun spraying is a form of thermal spraying which consisted of heating and directionally propelling powder on to the work piece from a combustion chamber by a stream of gas detonation products
  - Simple in design
  - Low porosity and high bond strength
  - Moderate substrate heating
  - High rate of growth of coating thickness
Detonation gun (D-gun)

Picture from www.gordonengland.co.uk/ds.htm
Temperature & Velocity
Thermal spray microstructure
Microstructures of ceramic TBCs by various processes

- **EB-PVD Deposited Coating**
  - Columnar grain boundary

- **Powder Thermal Sprayed Coating**
  - Lamellar splat boundary
  - Disk-shaped void

- **Liquid Precursor Sprayed Coating**
  - Vertical crack
  - Spherical void
Coating materials

- TiC
- TiN
- Titanium carbo-nitride
- Alumina etc.

Thermal spray gun
The most common control parameters

- Power input
- Arc gas pressure
- Gas pressure (He, H₂, N₂)
- Powder gas pressure
- Powder feed rate
- Grain size/shape
- Injection angle
- Surface roughness
- Substrate heating
- Spray distance
- Spray divergence
- Spray atmosphere
Vapor deposition techniques
PVD and CVD

Schematic Representation of Physical and Chemical Vapor Deposition

PVD

CVD

substrate

substrate

kinetic process at surface

complete pyrolysis on surface

partial pyrolysis in boundary layer
Chemical Vapor Deposition (CVD)

- **Chemical Vapor Deposition (CVD)** – กระบวนการเคลื่อนหรือการเกิดฟิล์มบางชั้นบนผิวชิ้นงานที่มีความร้อน ภายในบรรยากาศสำเร็จ และเกิดปฏิกิริยาทางเคมี ทำให้เกิดการถ่ายดน์ของแกสสู่ผิวของชิ้นงาน โดยมีการเกิด nucleate และ film growth โดยมีสารตั้งดินที่เป็นแกสหรือของเหลวระเหย เช่น Halides, hydrides

- **Applications of CVD**:
  - Resist → wear, corrosion and erosion of metal cutting tools, turbine and bearing
  - Protect → oxidation at high temperature
    - Integrated circuits;
    - Optoelectrical devices;
    - Micromachines;
    - Fine powders;
    - Protective coatings;
    - Solar cells;
    - Refractory coating for jet engine turbine blades.
CVD control parameters

☐ Pressure
☐ Temperature
☐ Reactant/product-activity
☐ Mass transfer
☐ Gas/vapor-flow dynamics
CVD reactor

- The reactant supply
- The deposition system
- Reactant/product retrieval
CVD → chemical reaction

- Thermodynamic (chemical reaction)
- Basic chemical kinetics (reaction rate)
- Mass and heat transfer (reactor and substrate size, design)
Basic steps in CVD (Jenson&Kern 1991)

- Reactants in gas flow –inlet-> deposition region
- Gas phase reaction -> film precursors + by products
- Film precursors → substrate surface
- Adsorbed on substrate
- Adsorbed precursors -> growth site or desorbed
- Surface reaction -> film + reaction products
- Reaction products -> desorbed from surface
- Desorbed products in the gas flow → outlet
Principle of CVD

- $3\text{SiH}_4 (g) + 4 \text{NH}_3 (g) \rightarrow \text{Si}_3\text{N}_4 (s) + 12 \text{H}_2$
- $\text{SiH}_4 (g) + 2 \text{H}_2\text{O} (g) \rightarrow \text{SiO}_2 (s) + 4 \text{H}_2$
- $2\text{AlCl}_3 (g) + 3 \text{CO}_2 (g) + 3\text{H}_2 (g) \rightarrow \text{Al}_2\text{O}_3 (s) + 3\text{CO} (g) + 6\text{HCl} (g)$
- $2\text{Al(CH}_3)_3 (g) + 8\text{O}_2 (g) \rightarrow \text{Al}_2\text{O}_3 (s) + 6\text{CO} (g) + 9\text{H}_2\text{O} (g)$
- $\text{Al(CH}_3)_3 (g) + \text{NH}_3 (g) \rightarrow \text{AlN} (s) + 3 \text{CH}_4 (g)$
- $\text{BCl}_3 (g) + \text{NH}_3 (g) \rightarrow \text{BN} (s) + 3 \text{HCl} (g)$
- $\text{SnCl}_4 (g) + \text{O}_2 (g) \rightarrow \text{SnO}_2 (s) + 2 \text{Cl}_2 (g)$
Principle of CVD

Carrier gas + reactants

Main gas flow region

Gas phase reactions

GAS

Transport to surface

Surface diffusion & Surface reaction

Redesorption of film precursor

Desorption of volatile surface reaction products

GAS

SOLID

Adsorption of film precursor

Nucleation & Island growth

Step growth

Carrier gas, unreacted reactants, by-products

Transfer of by-products to mainflow
How CVD Works

1. Mass transport of reagents to the deposition zone
2. Gas phase reactions in the boundary layer to produce film precursors and byproducts
3. Mass transport of film precursor to surface
4. Adsorption of film precursor on surface
5. Surface diffusion of precursor to growth site
6. Surface chemical reactions lead to film deposition and by-product desorption
7. Mass transport of by-product out reaction zone

- Main gas flow
- Gas Phase Reaction
- Transport to Surface
- Desorption of Precursor
- Nucleation and Island growth
- Step Growth
- Adsorption of Film Precursor
- Surface Diffusion
- Desorption of Volatile Surface Reaction Products
SiO$_2$
CVD system

Simplest Transport Analysis:
- reactant out / reactant in = 1: "differential reactor"
- reactant out / reactant in < 1: "starved reactor"

Gas / vapor source

Gas metering

deposition chamber

waste treatment

exhaust pump

water handling

Purge Panel

gas cabinet

MFC

gas in

gas out

to the outside world...

08/03/53
CVD reactor
Physical Vapor Deposition (PVD)

- **Physical Vapor Deposition (PVD)**
  เป็นกระบวนการเคลือบโดยเกิดจากไอของสารในสุญญากาศ โดยการเกิดไอของสารเกิดโดยอิオンของอาร์กอนชนกับวัสดุที่เป็นแคโทด และ อะตอมของวัสดุที่ต้องการเคลือบนั้นจะหลุดออกมาและไปตกตะกอนลงใหม่บนผิวชิ้นงาน

- **Evaporation**
- **Sputtering**
- **Arc Vaporization**
Applications of PVD:

- **Metals**, alloys, **ceramics** and some **polymers** may be deposited onto metals, ceramics and polymers by Physical Vapor Deposition method.
  - TiN, TiAlN, TiCN and CrN coating for cutting tools;
  - **AlSn coating on engine bearings**, diamond like coating for valve trains;
  - Coating for forming tools;
  - Anti-stick wear resistant coating for **injection molds**;
  - Decorative coatings of sanitary and door hardware.
PVD coating products
Steps of PVD (Bunshah 1982)

- Step 1: Creation of deposition species
- Step 2: Transport from source to substrate (collision + ionized)
- Step 3: Film growth on substrate (condensation, nucleation and growth)
Sputtering

The diagram illustrates the process of sputtering, which involves the removal of atoms from a target material by ion impact. The target (Cathode) is negatively charged, while the substrate is positively charged. Argon gas is used to create a plasma, which then impinges on the target, causing sputtering. The resulting atoms deposit on the substrate, forming a coating. 

www.substech.com
DC Plasma sputtering

- DC plasma sputtering
- Substrate/Anode: to be coated in cathode material
- Target/Cathode: containing raw material that is sputtered off by the positive ions impacts
- Background gas
- Neutral target atom
- Electron
- Ionized atom
- Negative Glow Plasma
- Cathode dark space (CDS)
Sputtering

E-beam

Laser ablation

Heat
# Evaporation process characteristics

<table>
<thead>
<tr>
<th>Method</th>
<th>Direct Evaporation</th>
<th>Gas Scattering Evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Vacuum Evaporation</td>
<td>Reactive Evaporation</td>
</tr>
<tr>
<td></td>
<td>Activated Evaporation</td>
<td>Activated Reactive Evaporation</td>
</tr>
<tr>
<td>Coatings produced</td>
<td>Single elements; alloys</td>
<td>Compounds</td>
</tr>
<tr>
<td></td>
<td>Alloys; compounds</td>
<td>Refractory Compounds</td>
</tr>
<tr>
<td>Evaporation source</td>
<td>Any suitable source; Single source for elements or alloys; wire or rod feed; Multiple source for alloys - but with reduced deposition rate.</td>
<td>Any source; usually electron beam</td>
</tr>
<tr>
<td></td>
<td>Usually electron beam</td>
<td>Usually electron beam</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Vacuum</td>
<td>Plasma</td>
</tr>
<tr>
<td></td>
<td>Reaction gas</td>
<td>Reactive gas &amp; plasma</td>
</tr>
<tr>
<td>Substrate</td>
<td>Floating, Grounded or electrically biased</td>
<td>As in Col.2</td>
</tr>
<tr>
<td></td>
<td>As in Col.2</td>
<td>Biased ARE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Enhanced ARE</td>
</tr>
<tr>
<td></td>
<td>Substrate is -ve biased; also called Reactive Ion Plating (RIP) Plating heating</td>
<td>Uses a thermionic electron emitter together with electron beam heating</td>
</tr>
</tbody>
</table>
Reactive evaporation
Reactive sputtering

- Compound growth on the target surface reduces the sputter rate.
- The reactive gas pressure rises.
- The film grows more slowly and so uses less reactive gas.

www.alacritas-consulting.com
Magnetron sputtering
Microstructure of coating

SEM cross-section:
10.5 µm thick alumina layer.
Pore size ~30 nm, pitch 100 nm. Co fi1led.
PVD reactor

Diagram showing the components of a PVD reactor, including the magnetron, motor, gas inlet, matching network, target, quartz chamber, Faraday shield, baffle, wafer chuck, and to pump. The diagram also includes the details of the power sources: magnatron 5 kW DC, 4-turn coil, ICP 1.8-2.2 MHz 2.5 kW, bias 13.56 MHz 1 kW.
# Process parameters & limitation of evaporation and sputtering process

<table>
<thead>
<tr>
<th>Process</th>
<th>Direct Evaporation</th>
<th>Reactive Evaporation</th>
<th>Activated Reactive Evaporation</th>
<th>Direct Sputtering</th>
<th>Reactive Sputtering</th>
<th>Magnetron Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Pressure Range, torr</td>
<td>$10^{-4}$-$10^{-5}$</td>
<td>$10^{-3}$-$10^{-4}$</td>
<td>$10^{-3}$-$10^{-4}$</td>
<td>$10^{-2}$-$10^{-3}$</td>
<td>$10^{-2}$-$10^{-3}$</td>
<td>$10^{-3}$-$10^{-4}$</td>
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<tr>
<td>Substrate Temperature, °C</td>
<td>500-1000</td>
<td>500-1000</td>
<td>room temp. -500</td>
<td>200-500</td>
<td>200-500</td>
<td>room temp. -500</td>
</tr>
<tr>
<td>Source-to-Substrate Gap, cm</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>5-10</td>
<td>5-10</td>
<td>5-20</td>
</tr>
<tr>
<td>Deposition Rate, Å/min</td>
<td>generally low; &lt;300 for compound films</td>
<td>generally low 200</td>
<td>&lt;500-10000</td>
<td>500 for compound films</td>
<td>up to 1000</td>
<td>up to 2000</td>
</tr>
<tr>
<td>Compound Dissociation</td>
<td>A major problem</td>
<td>limits dep. rates</td>
<td>Target poisoning</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comments</td>
<td>Difficult to deposit fully; low stoichiometric dep. rates</td>
<td>High temp. plasma control due to indep. pressure; energetic source power &amp; particle bombardment.</td>
<td>High dep. rates; High temp. gas pressure, substrate bombardment; source power &amp; surface state of target.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
VDO presentation

- Sputtering Process
- Plasma spray and thermal spray