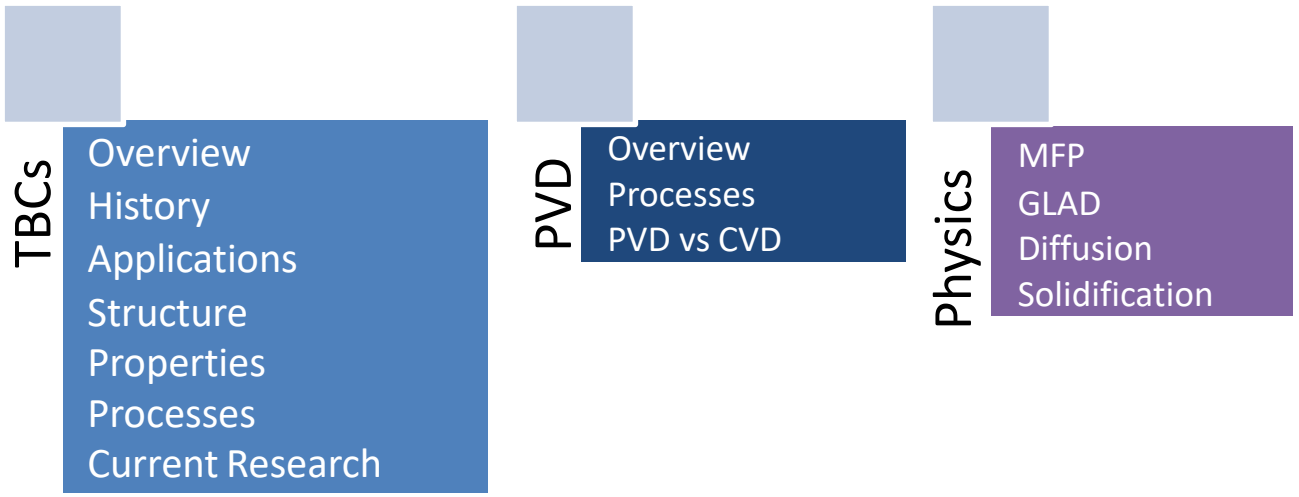
Thermal Barrier Coatings (TBCs)

Physical Vapor Deposition (PVD)

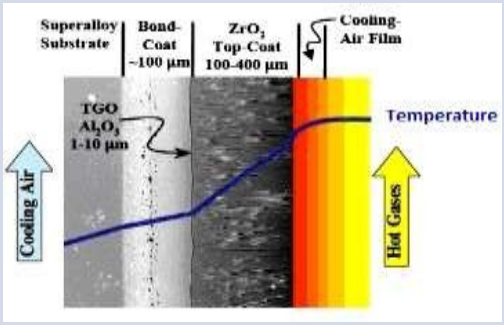
Outline


TBCs
Overview
History
Applications
Structure
Properties
Processes
Current Research
PVD
Overview
Processes
PVD vs CVD
Physics
MFP
GLAD
Diffusion
Solidification

Overview of TBCs

Purpose

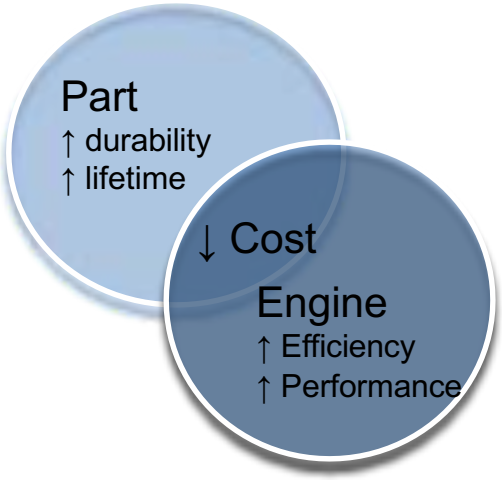
Provide thermal protection to metal parts exposed to hot combustion gases; allow hotter gases



Courtesy of Nitin Padture, The Ohio State University. Reprinted with permission from Padture, N. P., et al., Science (2002) 296, 280. © American Association for the Advancement of Science.

Function

- Improves engine technology



Features

- Low thermal conductivity
- Wear Resistance
  - Thermal
  - Corrosion
  - Mechanical
- Good bonding

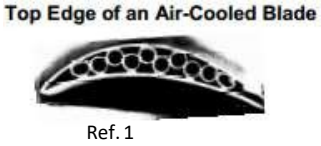
History

- **1910-20's**: Flame spraying developed (HVOF)
- **1948**: NBS tested frit enamel coatings in engines



Ref. 1

- **1940-60's**: Airforce leads development of frit coatings
  - Bad engine results, issues of durability
- **1953**: Blade lasted 100 hrs in engine test by Bartoo & Clure

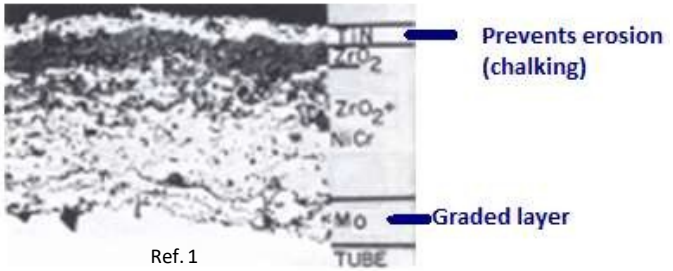


Ref. 1

- **1956**: LH2/LOX Rocket engine by NACA/NASA
  - NASA had a TBC group into the 1990's in Cleveland
- **1957**: First practical use of diffusion coating for turbine airfoil

History Continued

- **1960**: Rockide™ coating used in X15 rocket engine (XLR99 nozzle)
  - Prevented boiling of liquid ammonia coolant



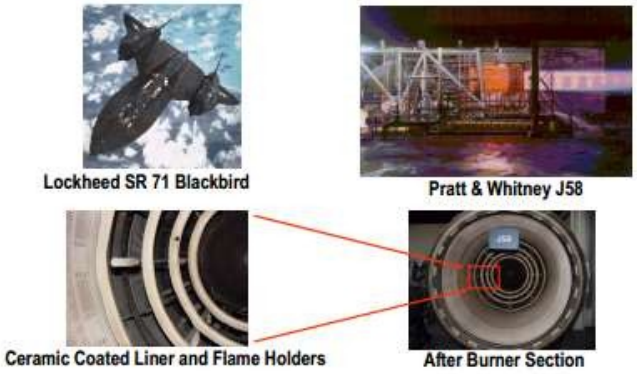
Ref. 1

- **1960 - early 70's**: Sal Grisaffe starts thermal spray research



Ref. 1

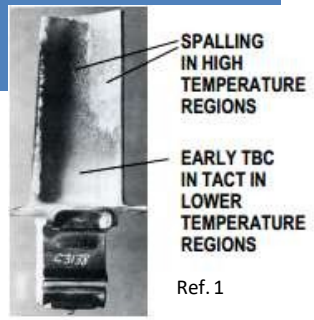
- **1970's**: Plasma sprayed coatings in commercial combustors



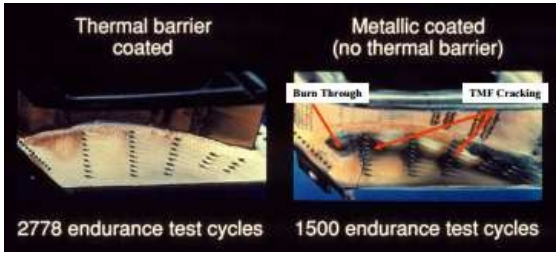
Ref. 1

History Continued

- **Mid 70's:** modern TBCs are developed (Liebert, Stecura, Jack Brown)
  - 12% yttria on NiCrAlY survived J-75 engine test
- **1977:** Advanced JT9D engine tests by P&W
- **1985:** P&W vane platform service life extended to 18,000 hrs
- **1989:** EBPVD coatings introduced into service



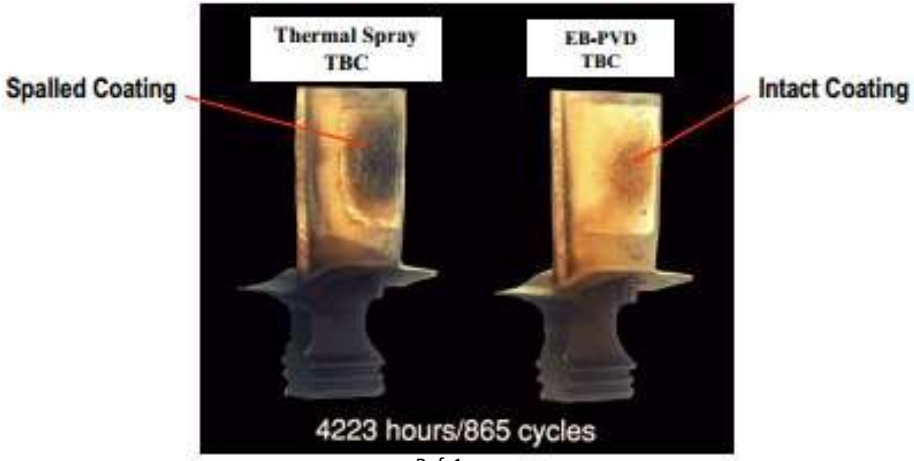
Ref. 1



Ref. 1



Ref. 1



Ref. 1

Applications

- Gas Turbines
  - Marine (ships)
  - Land based gas turbines
    - Electricity Generation—base load
  - Aerospace (jet engines)
  - Tanks
- Diesel engines (ICE)
  - Trains
- Braking systems
- Rocket engines
- Nuclear reactors
- Pump fluids



Ref. 3



Ref. 1



Ref.

Structure

100 – 300 µm	Ceramic top coat (6-9% wt. yttria-stabilized zirconia - YSZ) ↓ bond coat surface temperature by 100–200°C
1 – 10 µm	Thermally Grown Oxide- TGO(Al_2O_3)
130 – 300 µm	Metallic Bond coat Diffusion: NiAl w/ Pt group element doping Overlay: MCrAlY (M is Co and/or Ni)
3 – 7 mm	Substrate nickel superalloy (NiCoCrAlY)

Important TBC Properties

- **Erosion resistance**
  - Prevent spalling from water droplets or gas impurities: S & V or Calcium-Magnesium-Alumino-Silicate (CMAS)

- **Sintering resistance** (high temperature capability)
  - Important so ceramic layer maintains its as sprayed properties
    - High volume of pore space yielding strain tolerance & low thermal conductivity
    - Thermal stability of YSZ ceramic is up to 1200°C; new ceramic mat'ls are needed
    - The metastable tetragonal-prime (t') prime YSZ results in 4% damaging volume expansion, from monoclinic (m) to (t'), upon cooling

  - Simultaneously modifying the rotational speed & the deposition temperature showed low Young's modulus and low tendency to sinter (EBPVD).

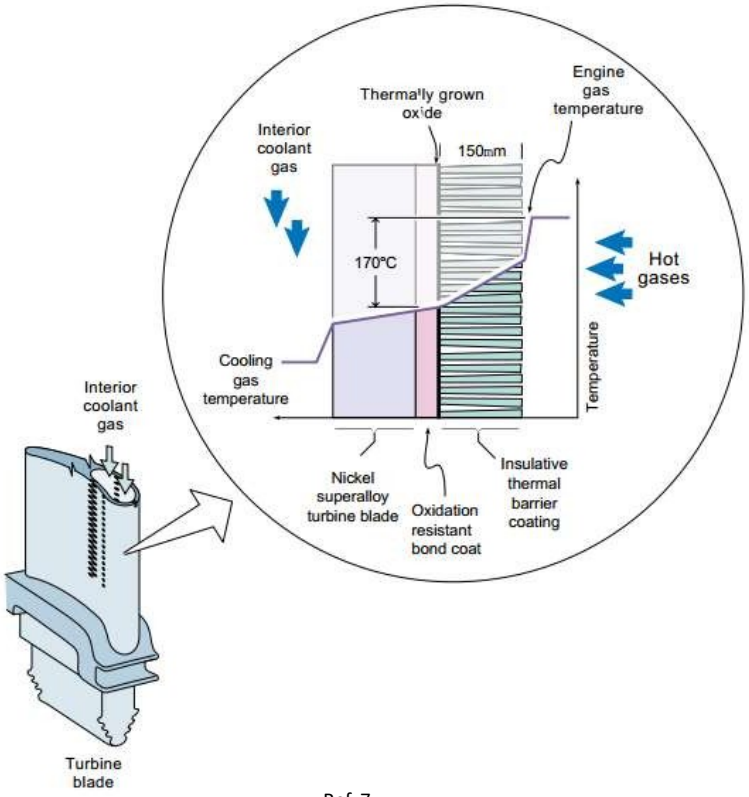
- **Strain compatibility**
  - Similar thermal expansion coefficients of metallic bond coat/TGO & ceramic

- **Chemical compatibility**

- **Corrosion/oxidation resistance**

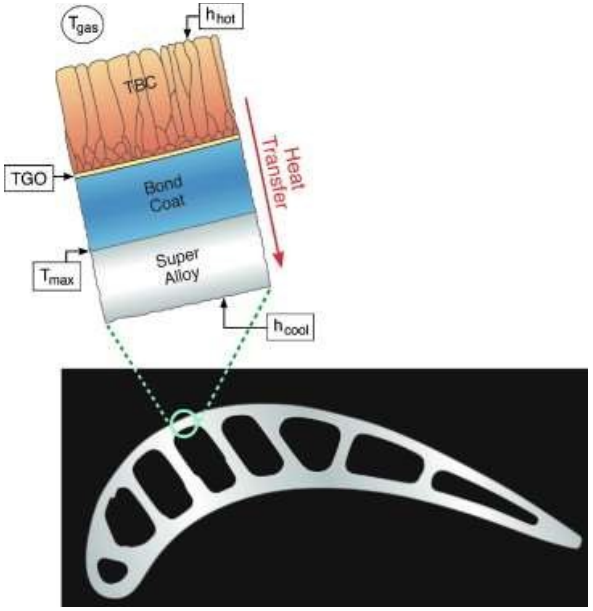
- **Thermal mechanical fatigue (TMF/TCF) resistance**

Structure



Ref. 7

A schematic of an airfoil and a magnified view of a surface zone with the thermal barrier coating (TBC) and bond coat layers identified.



Ref. 6

Processes

Physical Vapor Deposition (PVD)

Vapor deposition or condensation

Electron Beam PVD (EBPVD)

50 – 100 µm/min

Ion Enhanced EBPVD (IE EBPVD)

Thermal Spraying

Melted or heated powder

Air-Plasma Sprayed (APS)

Cleaner & lower cost

H & Ar plasma, 350 – 560 m/s

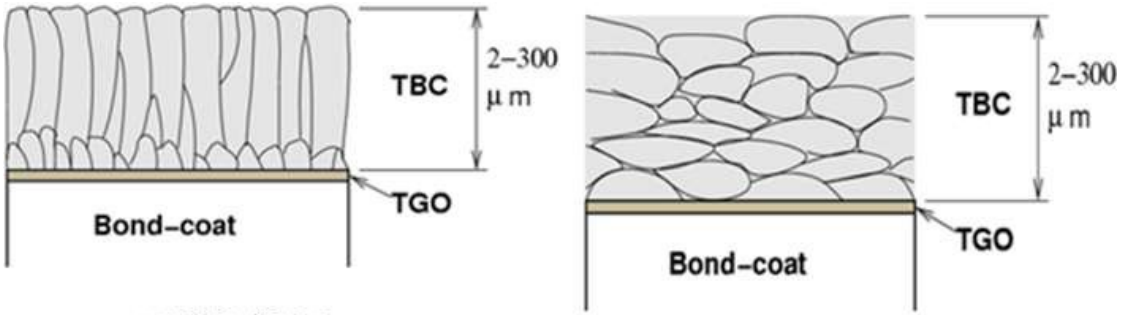
High Velocity Oxy-Fuel (HVOF)

Better oxidation resistance of bond coat & simpler

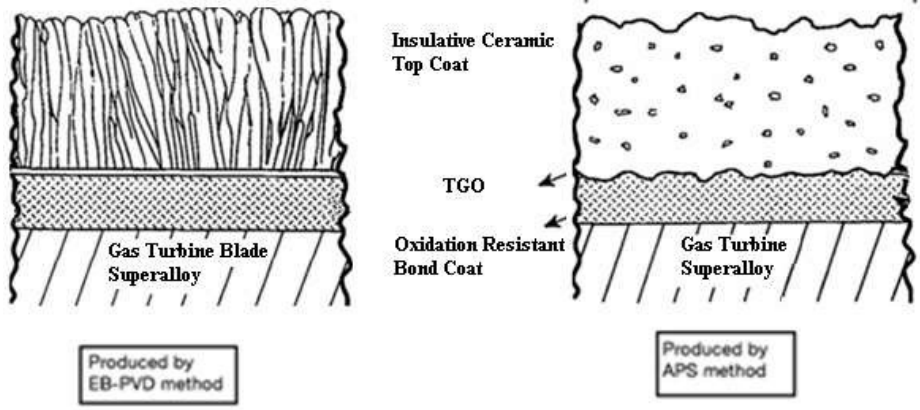
Liquid or gaseous fuel & O combust, 700 m/s

EBPVD APS

Ref. 9



Ref. 7



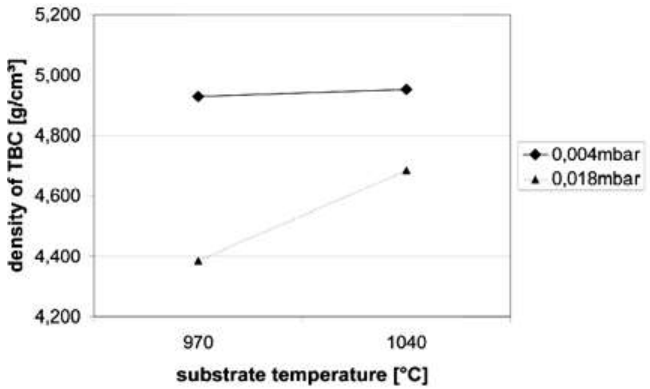
Microstructure

- 10-15% voids offers good durability
- low density offers 15% ↓ thermal conductivity

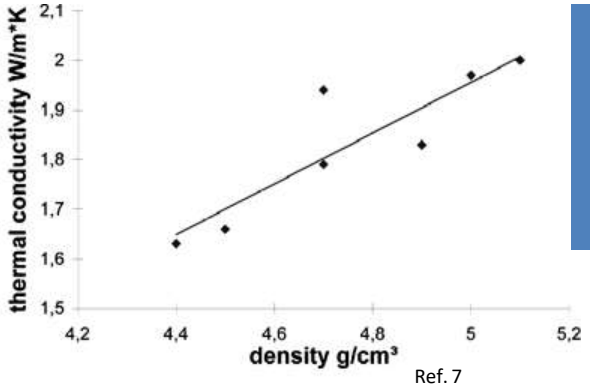
Last 8-10X longer before spalling; better adhesion
More uniform, dense, lower surface roughness
Gradient structures possible
Cooling holes remain open

Lower thermal conductivity
• APS at 0.6–1.2 W/mK, EBPVD: 1.8–2.0 W/mK
Better corrosion resistance
Better understanding
Multilayer splat structure
Wider composition range
Lower fracture toughness

Thermal Conductivity (EBPVD)



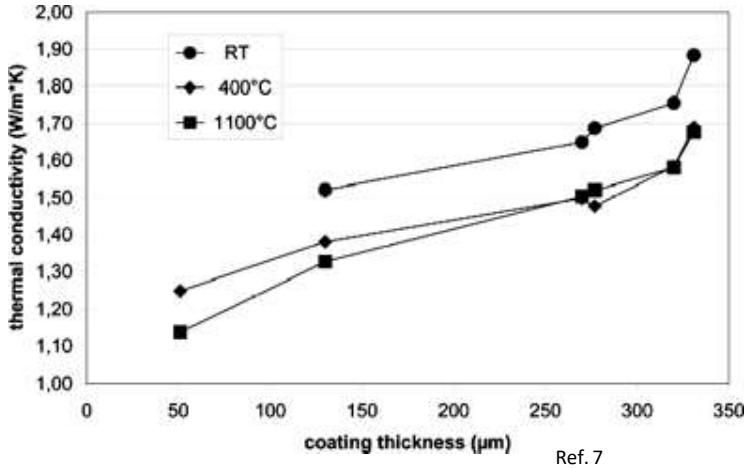
a)



Ref. 7

b)

(a) Density as a function of process parameter (chamber pressure and substrate temperature)
(b) Thermal conductivity as a function of density



Ref. 7

Thermal conductivity as a function of thickness.

- 35% reduction for 52 µm vs 350 µm layer
- Inserting & withdrawaling the sample carrier yields ↓ 20% in thermal conductivity (mostly due to temperature fluctuations, not the thin layers)

Measurements were done after an initial 2 h/1080°C heat treatment.

Current Research

- Failure mechanism for a TBC is thermal fatigue and oxide growth; >10 µm TGO thickness = failure.

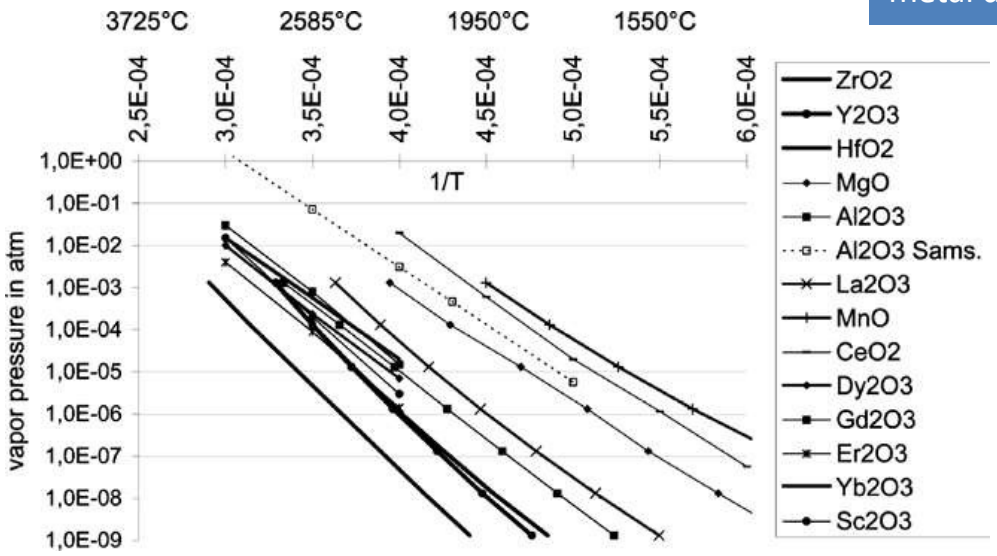
- Oxidation resistance, not spallation, has become concern. Porous ceramic layer produced by EBPVD offers little to no corrosion resistance.

- **Early 1990s:** focus shifted to low thermal conductivity of ceramic topcoats, APS offers low thermal conductivity but poor durability.

Ceramic Mat'ls

Vapor Pressures of Various Oxides as a Function of Inverse Temperatures

Ceramic Rare-earth metal dopants



Ref. 8

Overview of PVD

- PVD processes take place in a vacuum chamber and require a thermal energy (heat) source to vaporize or an ionized plasma to eject target material.
- Vacuum
  - Removes air (oxygen)
    - ↓ O point defects
    - ↓ scattering
    - ↑ density (However, sputtering is done at low vacuum but has high density due to the high energy input.)
  - Helps transport evaporant
    - Growth is 1-10 nm/sec

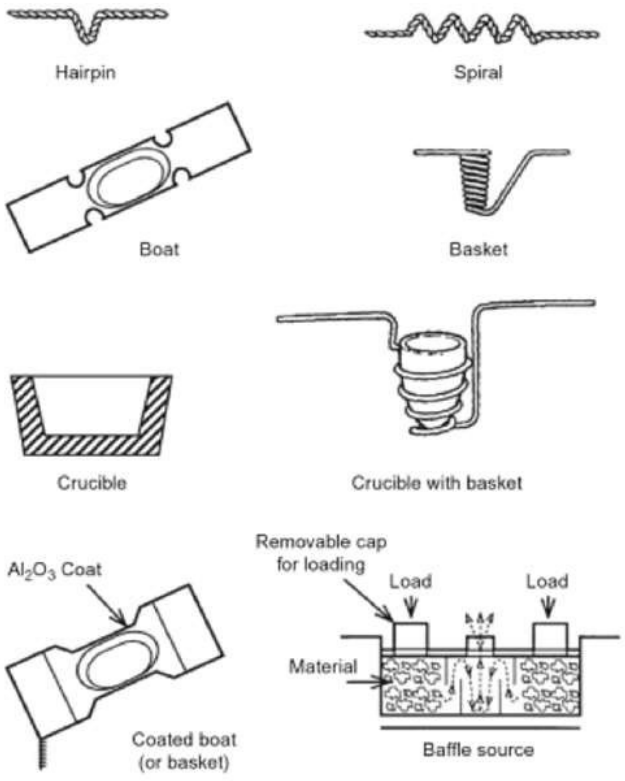
Processes

- Evaporation
  - Resistive
  - Electron Beam
- Pulsed Laser Deposition/ Cathodic Arc (Arc-PVD)
- Sputtering
- Ion Plating (aka Ion assisted deposition (IAD) or Ion vapor deposition (IVD))
  - Plasma is used to clean the substrate (“backsputtering”) before deposition and modify the film during deposition (“resputtering”).

Thermal PVD

- Aka Evaporative PVD or Vapor PVD
- Vaporizing mat'l at temperatures <1500°C & vacuum >10^{-4}
- 0.1-0.3 eV
- Filament (charge rod) is a refractory of either W, Ta, Mo, C, or BN/TiB_2 & melts the source rod

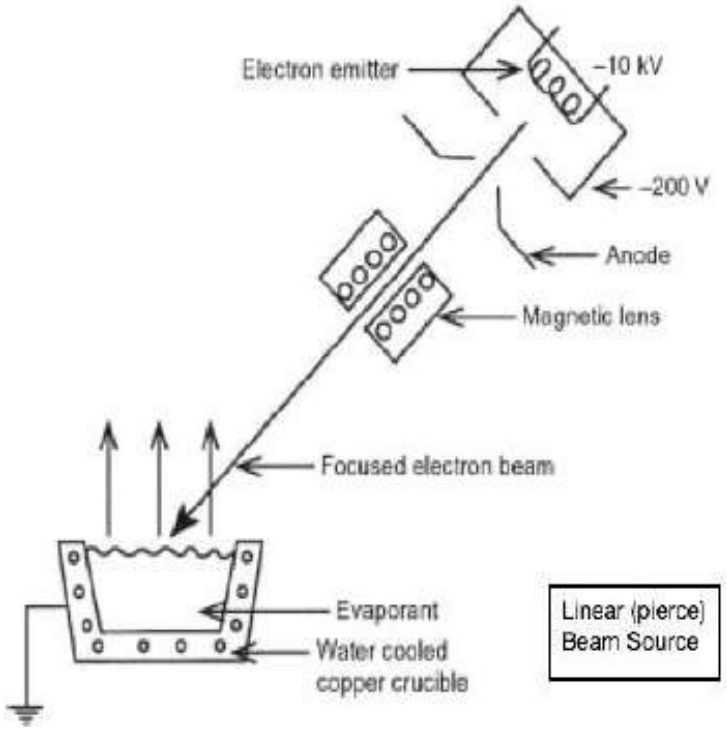
Resistively Heated Thermal Vaporization Source Configurations



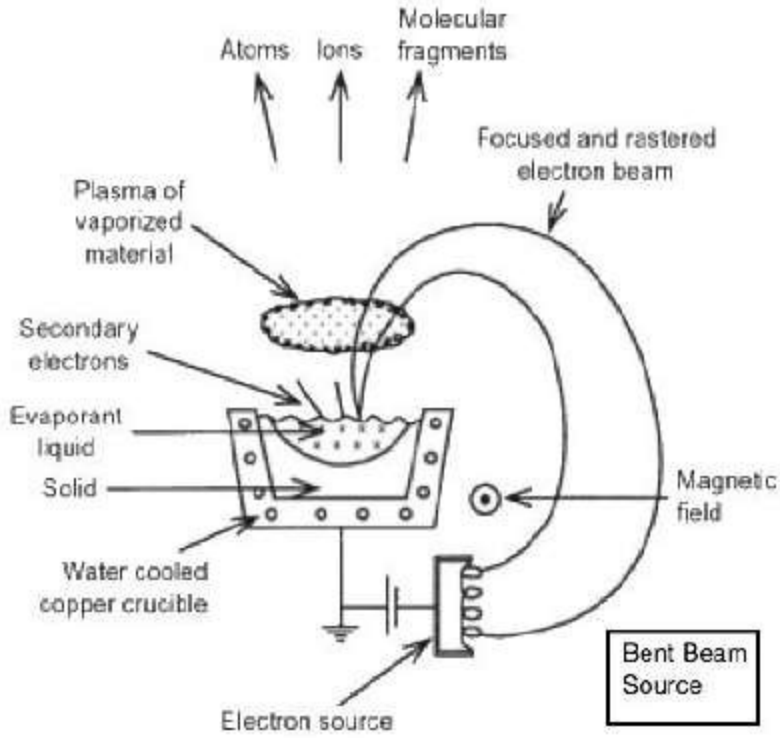
Ref. 10

Electron Beam-PVD (EB-PVD)

Vaporizing mat'l at temperatures >1500°C
Electron beam penetrates a few µm depth
Vacuum >7.5 X 10-5 Torr – to pass e-'s & ionized gas.
High current (> 10^{10} A/cm2), low voltage (10-30 V)

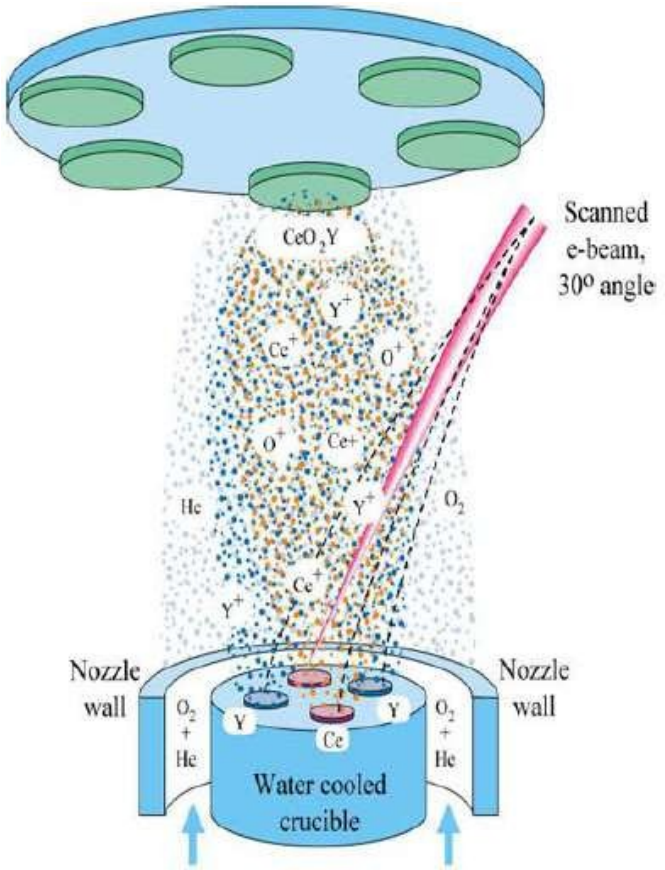


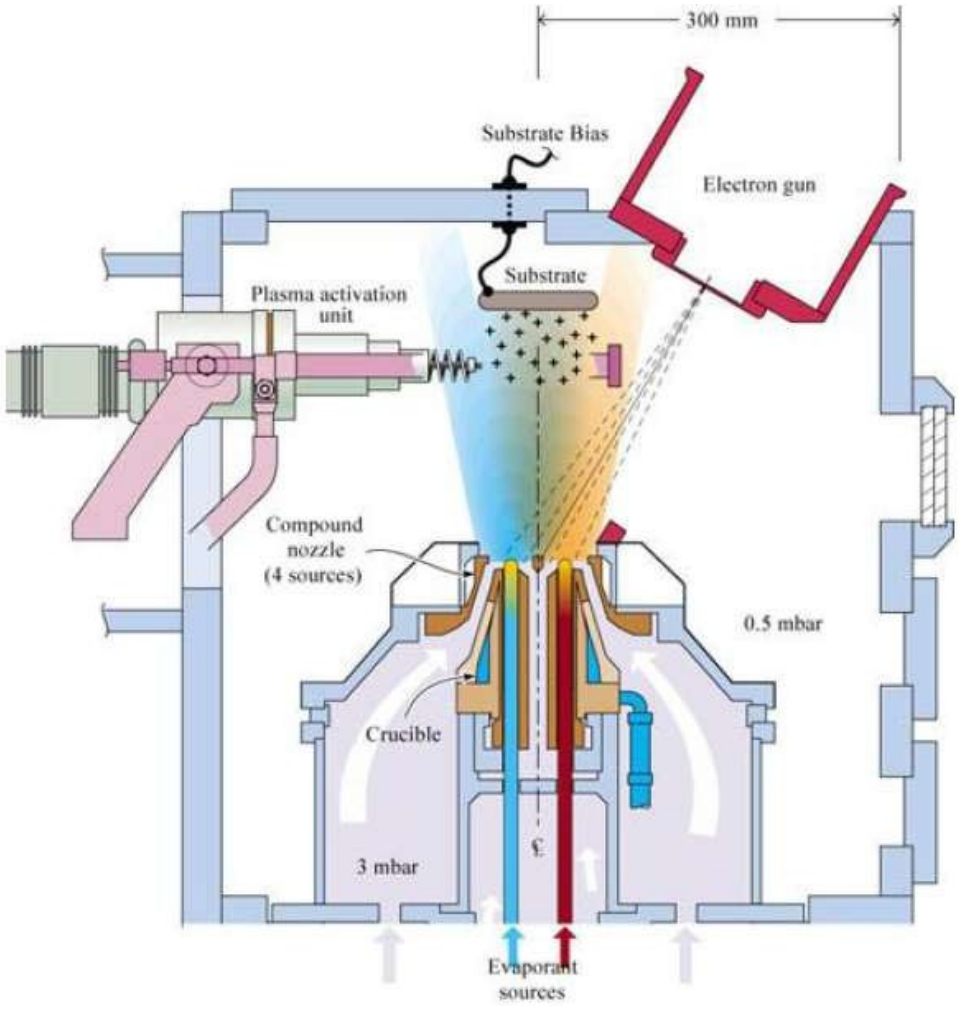
Ref. 10



Ref. 10

EB-PVD Continued





Pulsed Laser Deposition

Vacuum (10^{-3} – 10^{-7} Torr)

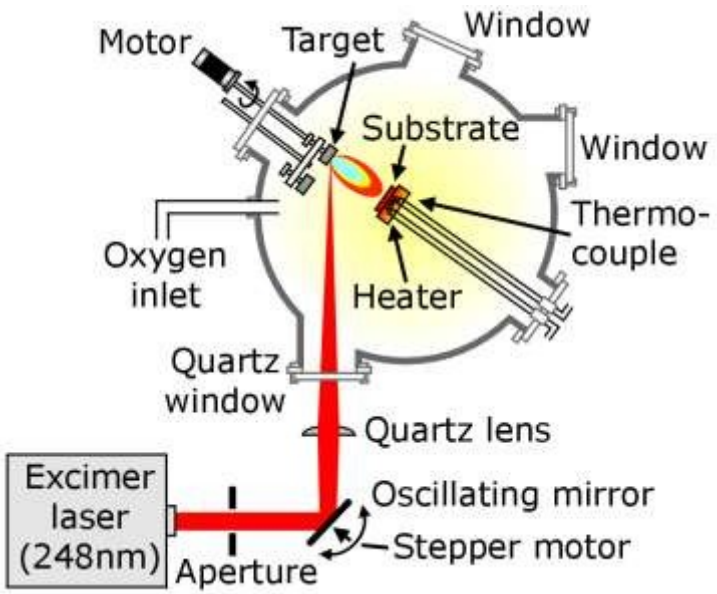
Laser beam

- Excimer laser - UV
  - Ionized gas (i.e. Ar^+) generates photons: massless, chargeless, carries & responds to EM field
  - Depends on optical absorption coefficient of target material
- Pulsed energy method
- Penetrates 0.25 µm depth

Cathode spot:

- Size of a few µm
- Temperature of 15,000°C
- Yields high velocity (100 m/s) jet
- High current density of 10^6 - 10^{12} A/cm^2
- Self-sustaining plasma (>85% ionized, 10-100 eV)

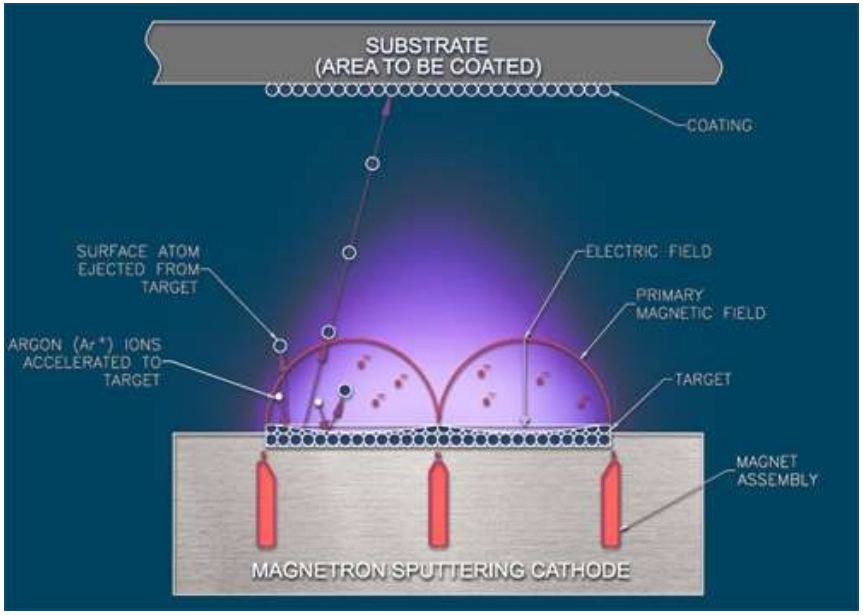
- Pulsed Electron Deposition (PED)
  - Deposits complex material
  - High power density (~10^8 W/cm^2)
  - 100 ns, high I, low V (1,000 A, 15 keV)
  - Penetrates 1 µm depth



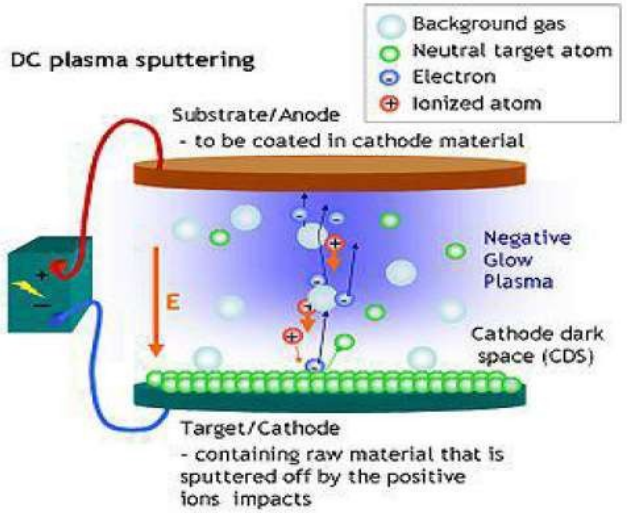
Ref. 11

Sputtering

- Plasma: Ar-H or Ar-He is ionized using e-field (Reactive sputtering using O), low vacuum 10^{-1} - 10^{-3} Torr
- Few eV- 10's eV
- Compared with EBPVD: higher stresses in film and slower deposition rates
- Greater variety of mat'ls: ceramics, metals, & alloys, not relying on reaching vaporizing point.
- Sputter deposit thin ceramic layer ("primer" film), then plasma spray rest of ceramic.

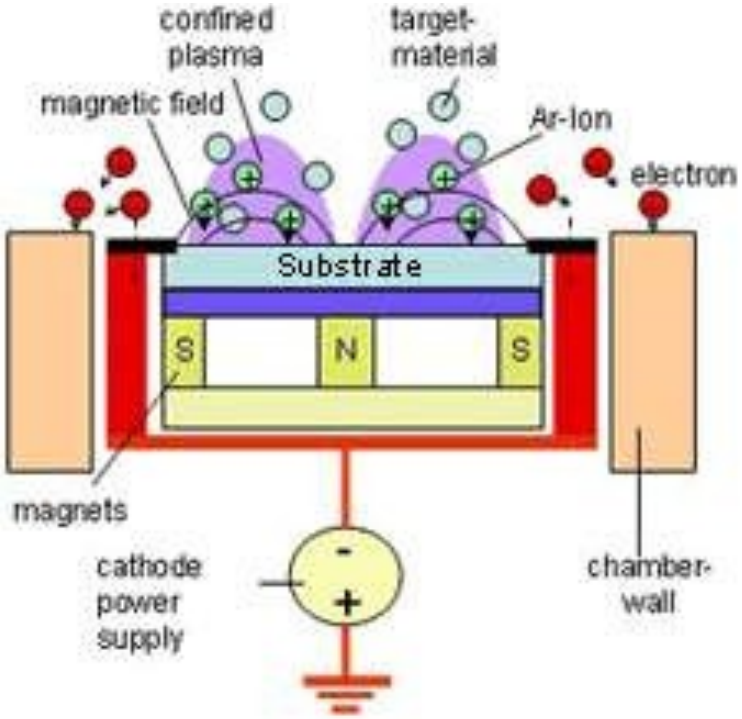


Ref. 12



Ref. 12

Sputtering Continued



Ref. 12

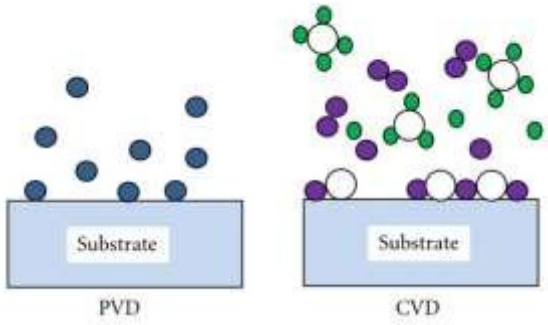
PVD vs CVD

High temperature (>800^{o}C vs 200– 500°C) decomposition or reduction of a chemical vapor precursor

Higher temperature results in more diffusion bonding, giving the metallic layer better adhesion.

Chemical reactions in CVD result in corrosive volatile byproducts and unused reactive gas that must be removed by gas flow from the chamber.

Uses gases, evaporating liquids, & chemically gasified solids as the source



Ref.

Physics: Mean Free Path (MFP)

- Distance an atom travels before colliding with another atom

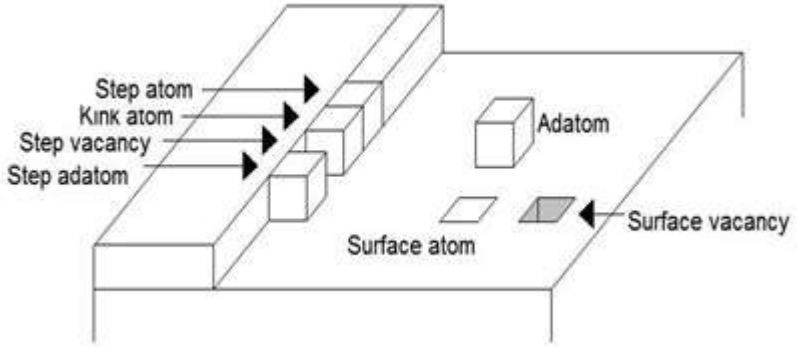
- Vacuum >10^{-4} Torr for a distance between source and target of 10-16’’

Glancing Angle Deposition (GLAD)

- Columnar growth in direction of flux
- Rotating substrate during GLAD results in a corkscrew microstructure with 40% reduction in thermal conductivity

Diffusion

- Adatoms- mobile atoms that lie on the substrate.
- Mobility of adatom (i.e. diffusion) depends on its energy, chemical reactivity with surface atoms, and temperature of the substrate.
- Ballistic deposition- no mobility
- Increase mobility by
  - Increasing substrate temperature
  - Ion-bombardment



Ref.

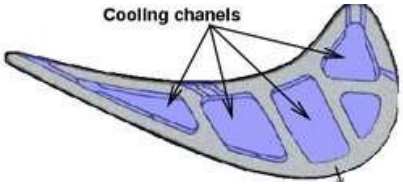
The names for the various atomic positions in the TLK model. This graphic representation is for a simple cubic lattice.

Solidification

- Plasma spraying
  - Rapid solidification occurs when liquid particles (some vapor) strike the substrate surface
  - Flatten and cool (10^6K/sec) to form splat
  - Fine, non-columnar (i.e. equiaxed grains) structure
  - Lamellar structure parallel to substrate
- PVD
  - Solidification results in columnar growth
  - Elongated grains normal to substrate
  - Cooling deposit slowly- nucleation of new crystals is less than at large under cooling yielding large dendrites
- Plasma spray-PVD (PS-PVD) is a combination of Low Pressure PS (LPPS) and PVD. There is both molten feed stock that forms splats & vapor transported in a supersonic plasma plume to condense.

Conclusion

- TBCs are applied to Ni-based super alloy turbine blades that have internal air cooling channels.
- Ceramic Matrix Composites- GE is replacing certain hot section metal components with ceramic mat'l
  - Better temperature capability; ↑ durability of 30,000 hours
  - 1/3 the weight of Ni
  - Entry into service: 2016: Airbus A320neo, 2017: Boeing 737max
- Cooling
  - Air convection- 370°C (1-3% of compressor air)
  - TBCs- 100 – 200°C
  - Single crystal blades and directional solidification- 120°C
- Multi-layer (i.e. micro-layering)
  - One method of layering, at a thickness of 1 µm, is to switch on and off a bias voltage.
  - Produces layers of different density yielding a 37-45% reduction in thermal conductivity





Ref.

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12. I. Lubomirsky. "Ceramic Thin Films: Piezoelectric, Ferroelectric, Ion-Conductors." *Materials and Interfaces*

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14. "Vacuum Turbine Blade Coating." *ALD Vacuum Technologies*

Other Books in the Deposition and Coatings Subject Area

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0-8155-1442-5 • Krishna Seshan • 2002

Handbook of Physical Vapor Deposition (PVD) Processing
0-8155-1422-0 • Donald M. Mattox • 1998

Handbook of Chemical Vapor Deposition, Second Edition
0-8155-1432-8 • Hugh O. Pierson • 1999

Electrodeposition: The Materials Science of Coatings and Substrates
0-8155-1320-8 • Jack W. Dini • 1992

Handbook of Sputter Deposition Technology
0-8155-1280-5 • Kiyotaka Wasa and Shigeru Hayakawa • 1991