# PHS6317 - Nanoingénierie des couches minces - Nanoengineering of thin films

Thermal spray processes and coatings

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Polytechnique Montréal, February 9, 2024

# Outline

- Introduction to thermal spray processing

- Plasma spray
  - Air plasma spray
  - Suspension plasma spray

- Combustion processes:
  - Flame
  - HVOF / HVAF

- Arc Spray

- Cold spray / Kinetic spray

- Applications

# References

- Maher I. Boulos, Pierre L. Fauchais, Joachim V.R. Heberlein,, **"Thermal Spray Fundamentals: From Powder to Part "**, 2nd Edition, Springer, 2021, 1136 p

- **ASM Handbook, Volume 5A: Thermal Spray Technology**, Robert C. Tucker, Jr., Ed., 2013, 412 p.

- L. Pawlowski, **"The Science and Engineering of Thermal Spray Coatings"**, Wiley, 2008, 656 p
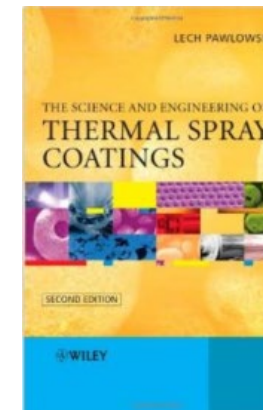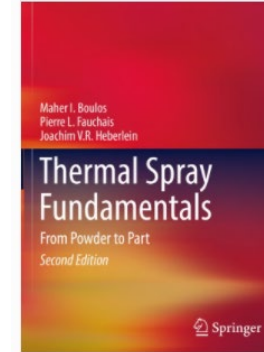
# What Is Thermal Spraying?

- **A family of processes in which a finely divided surfacing material is sprayed in a molten or semi-molten state on a prepared substrate to form a coating**.
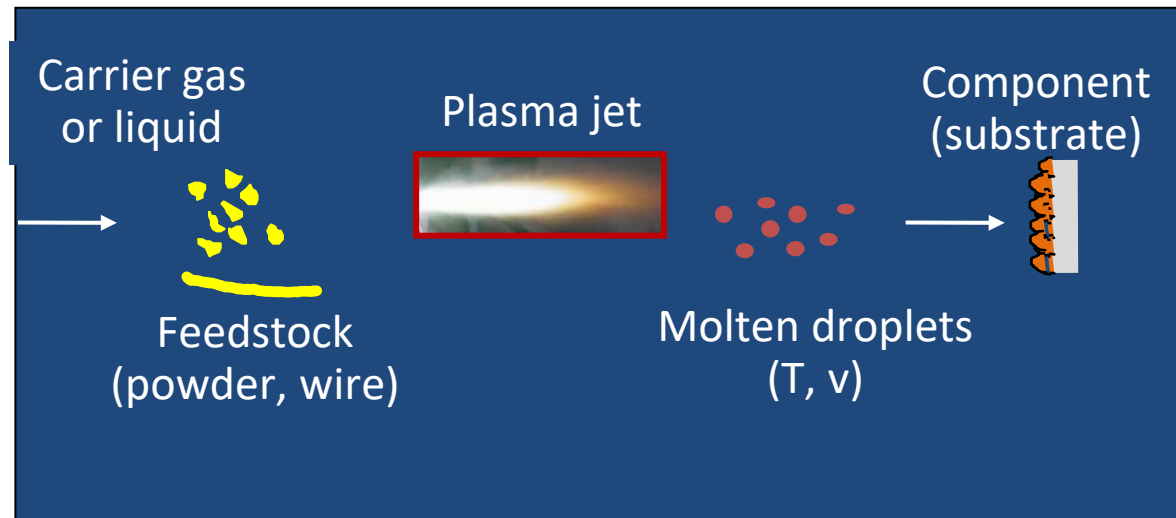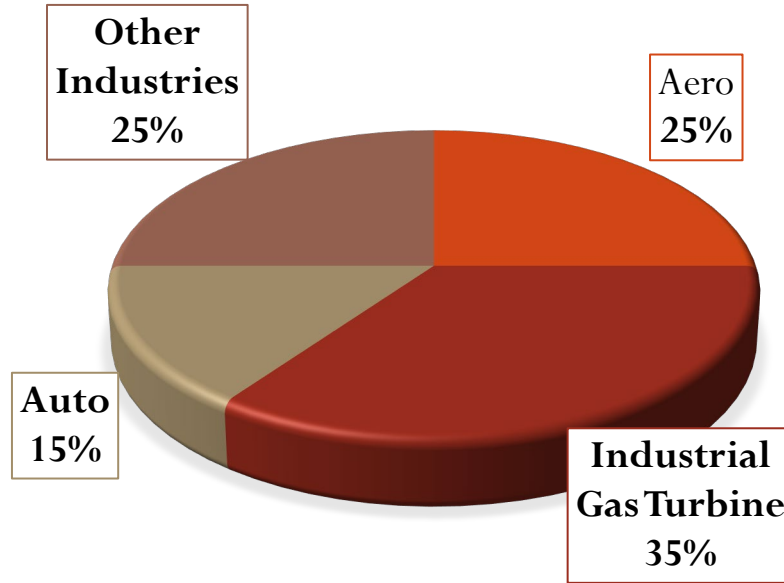
# What Is Plasma Spraying?

- The flame is a thermal plasma jet heated by a high intensity dc current arc between the anode and cathode (300-800 A, 30-80V)



Powder feeding

Substrate

Plasma

Coating

Plasma gas
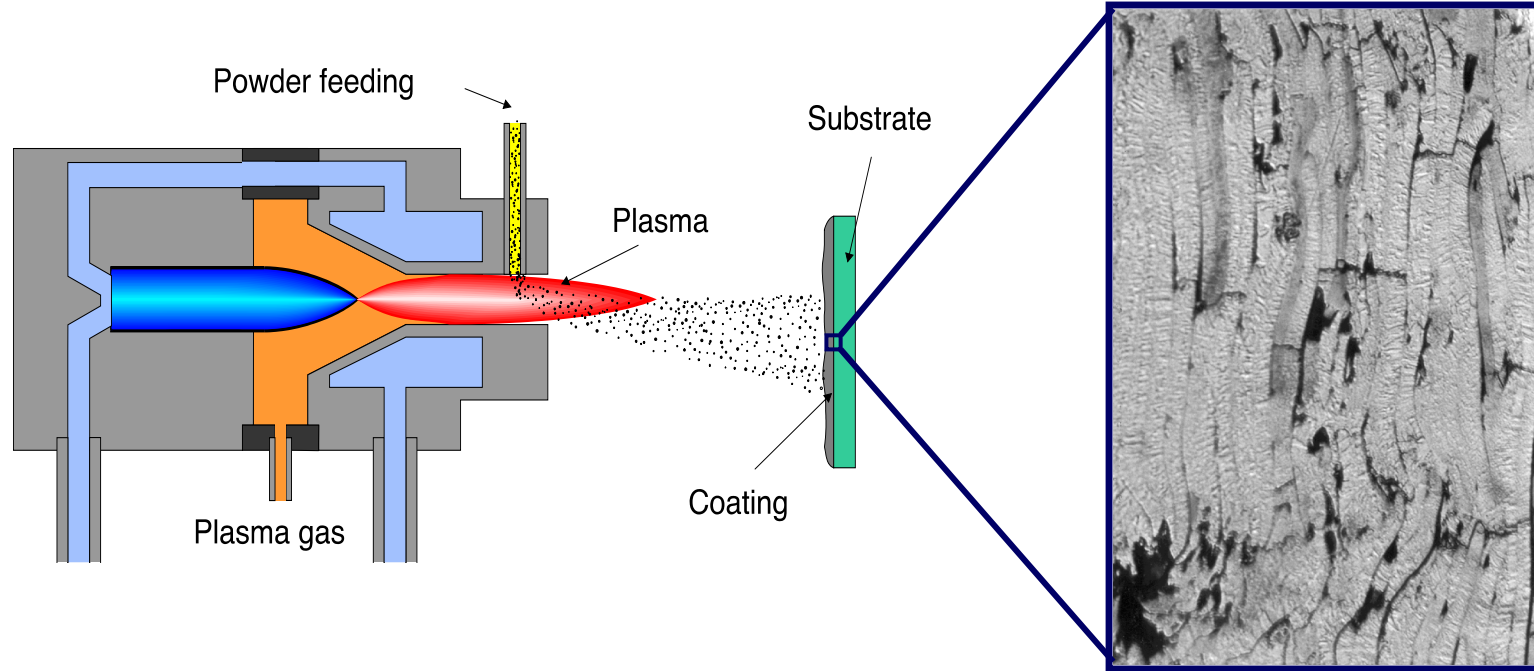
**Coating cross-section showing the lamellar structure**

# Thermal Spray Markets

❑ Global market estimated at $7.5 billion US(Dorfman, MS&T 2011)



**Other Industries**
25%

**Aero**
**25%**

**Auto**
15%

**Industrial Gas Turbine**
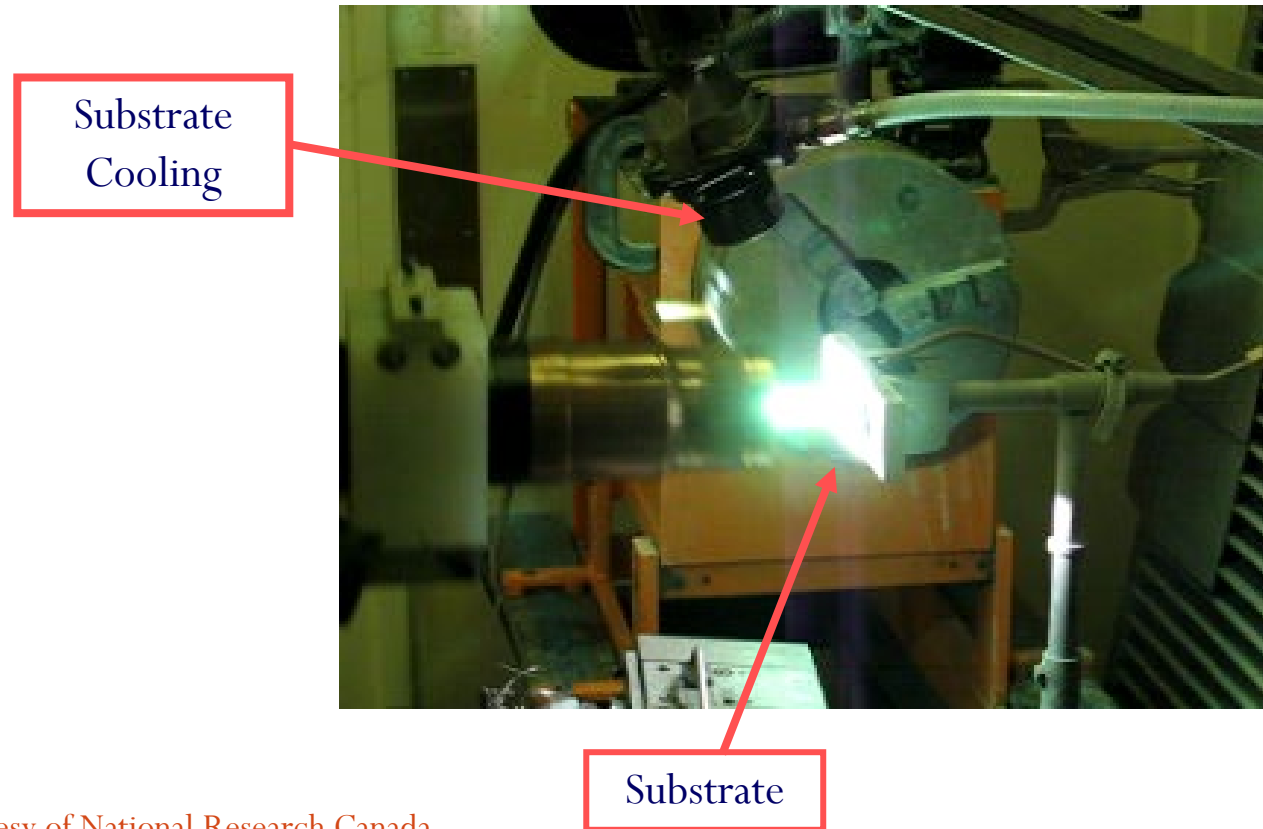**35%**

**Other Industries**

- Printing, pulp and paper
- Biomedical
- Mining, metal processing
- Petrochemical
- Electronics
- Etc.



*Images courtesy of NRC Canada

# Plasma Spraying

- The plasma torch is scanned in front of the substrate as many times as necessary to get the required coating thickness (10 microns – millimetres)
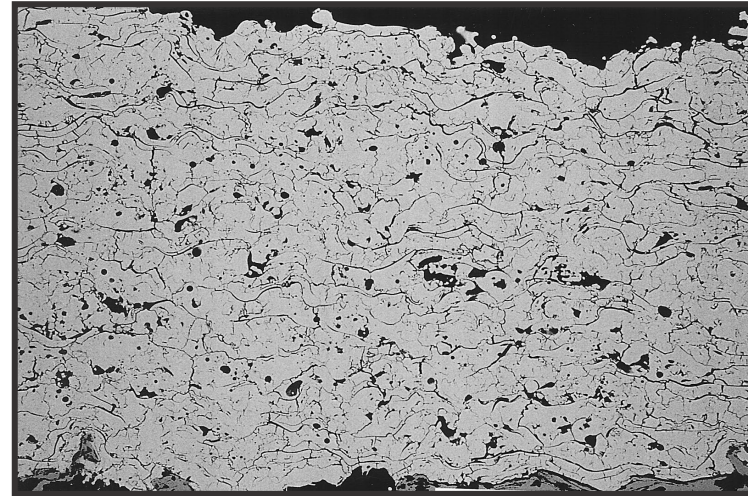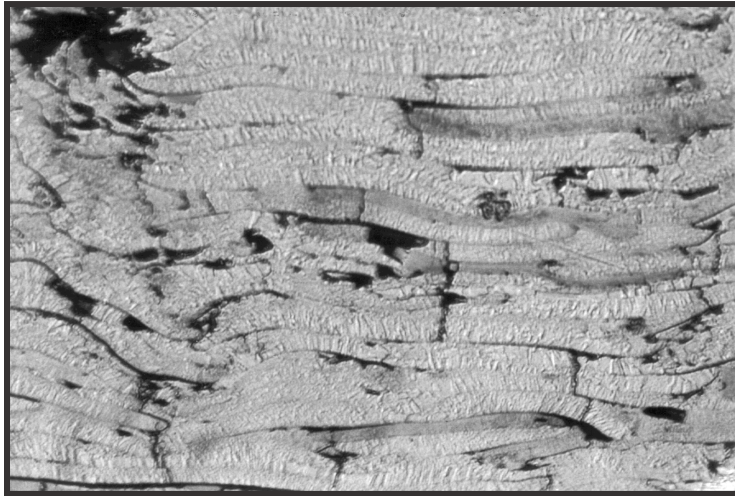


Substrate Cooling

Substrate

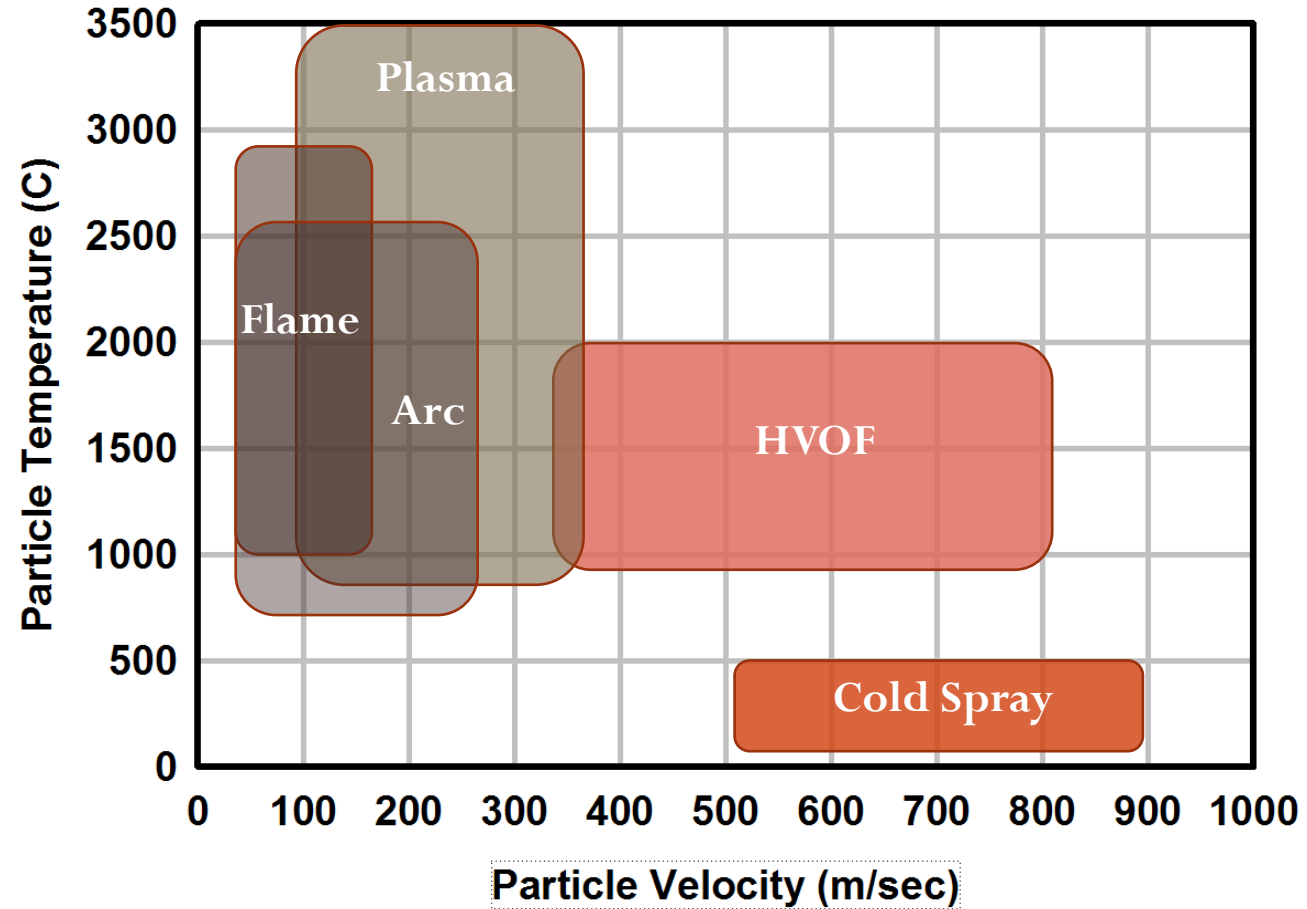*Image courtesy of National Research Canada

# Coating Structure

- Coatings are built by the accumulation of molten or partially molten particles impacting on the substrate surface

- Lamellar structure
- Pores and cracks

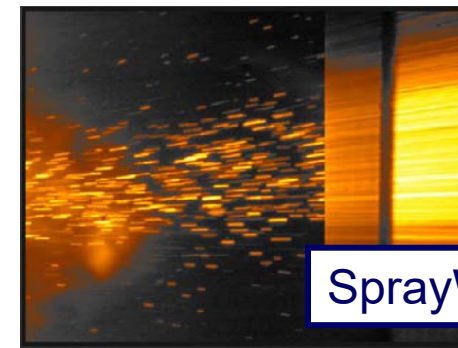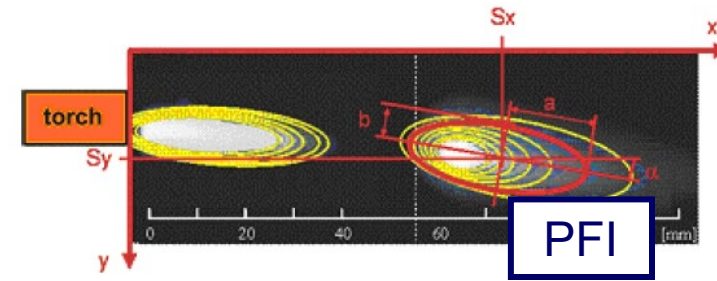# Thermal Spray Processes: Particle Characteristics

# In-flight Particle Diagnostics: Commercial Sensors

- Detection of thermal radiation emitted by the hot particles
- Camera for monitoring the orientation, width and intensity of the particle jet
- Commercial systems for monitoring particle jet characteristics:
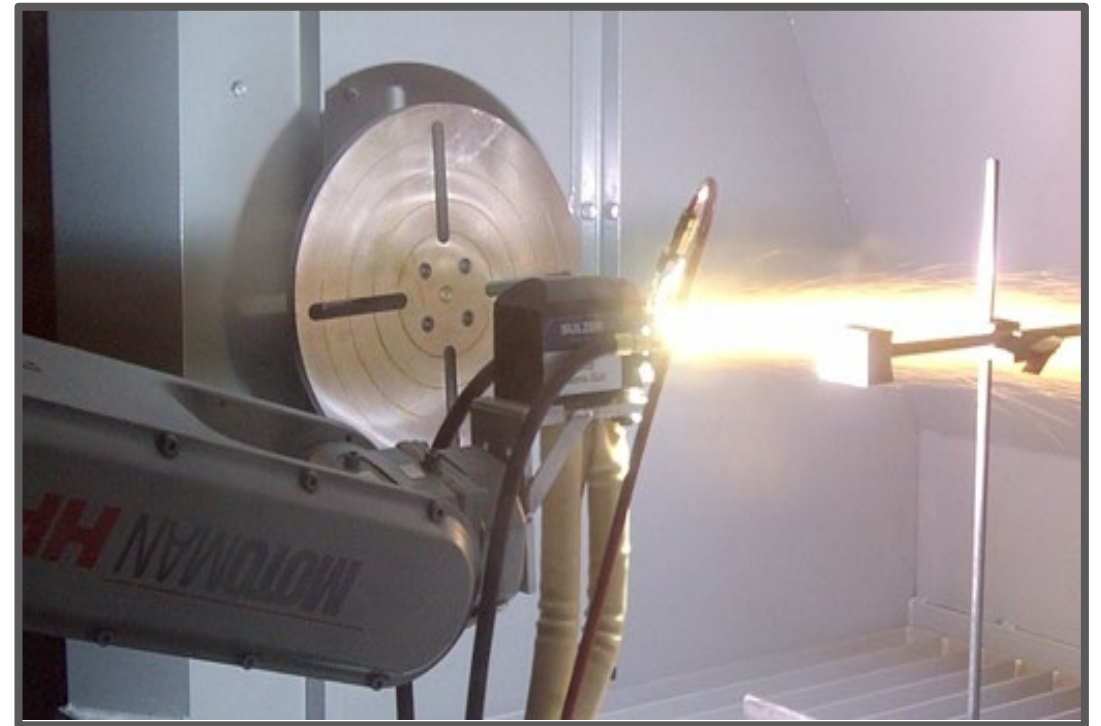
Accuraspray/PlumeSpector

DPV 2000

PFI

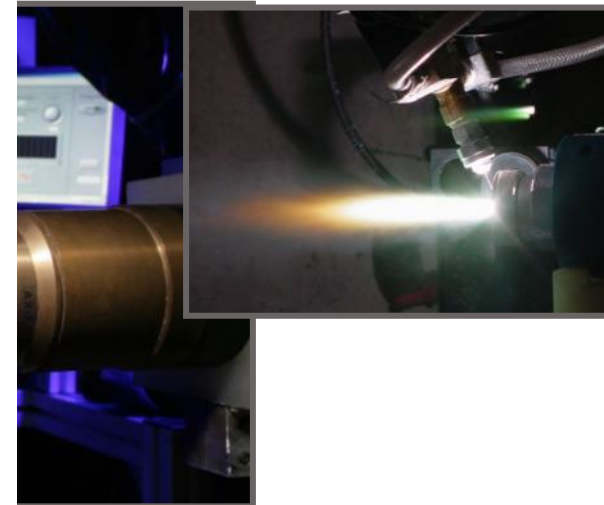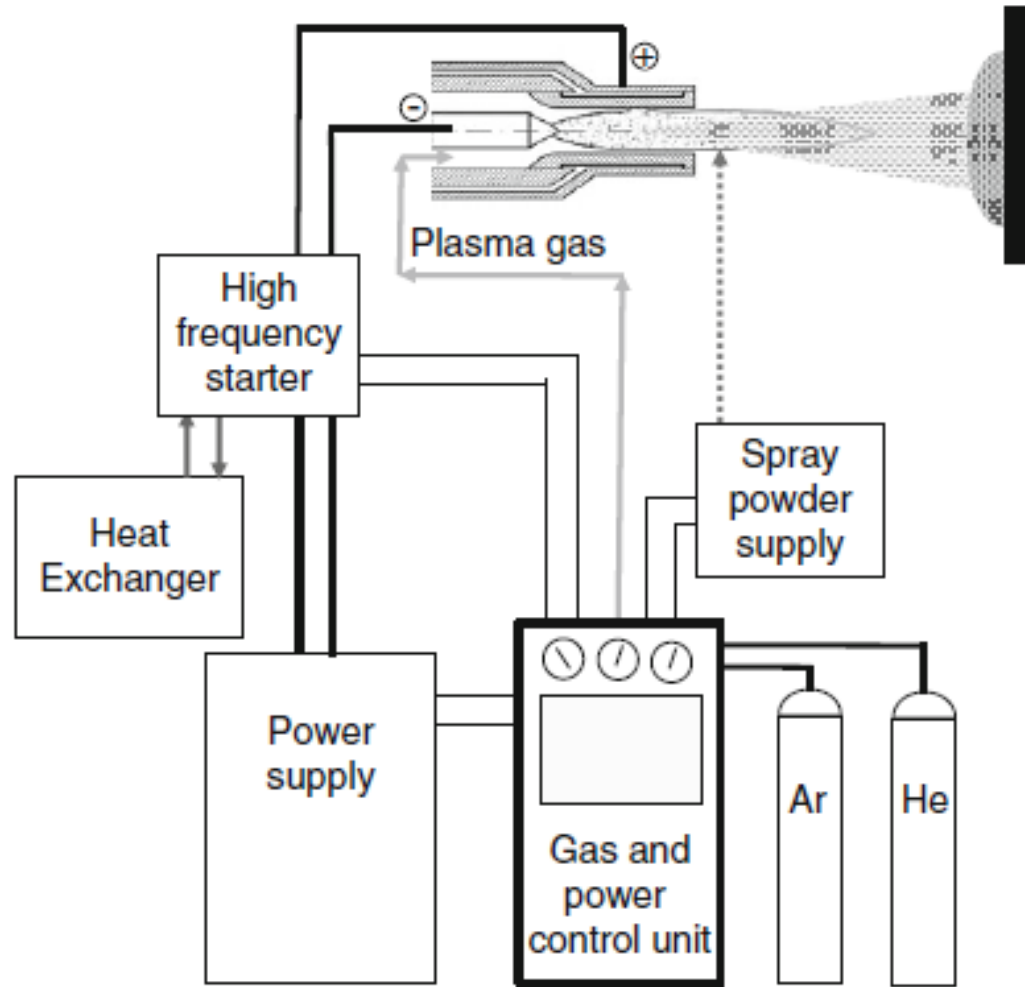SprayWatch

# Plasma Spray

# Plasma Spray

Air Plasma Spray
Concordia

# Plasma Spraying

- Particle characteristics
  - temperature ~ 800-3500°C
  - speed ~ 100-350 m/s
- Materials - ceramics, metals and cermets
  - deposition efficiency ~ 30 to 70 %
  - spray rate ~ 1 to 3 kg/hour
- Coating characteristics
  - density ~ 5 to 20% porosity

- The plasma temperature reaches 10,000K and more. Thus any material that can melt without decomposition or sublimation can be sprayed
  - Well adapted for ceramics and refractory metals

# Spray Parameters

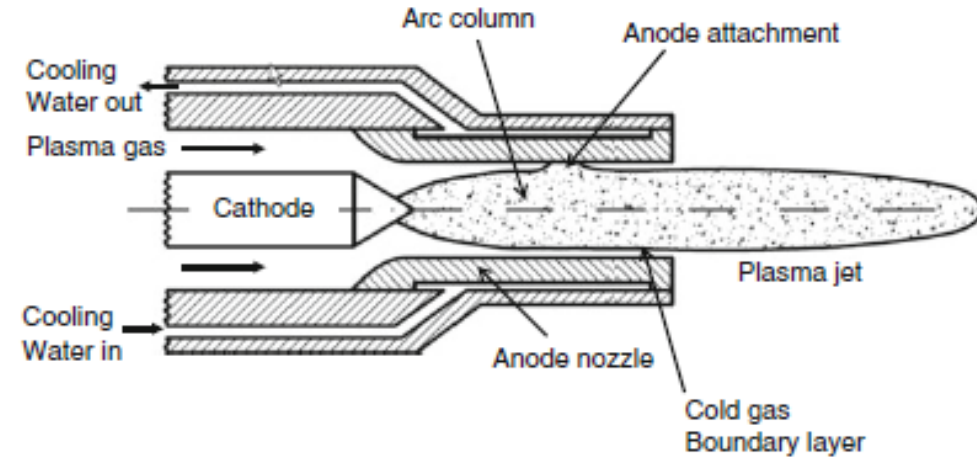| Parameters | Torch | Plasma Jet | Spray Particles | Substrate |
|---|---|---|---|---|
| Input | • Current<br>• Primary and secondary gas flow rate<br>• Cooling water flow | | • Feed rate<br>• Carrier gas flow rate | • Surface preparation<br>• Heating/cooling<br>• Motion relative to the torch<br>• Spray distance |
| Operating | • Voltage<br>• Voltage fluctuations<br>• Thermal efficiencies | • Plasma jet T and v<br>• Plasma jet stability | • Particle injection speed<br>• Particle trajectories<br>• Particle T, v and flux | • Substrate temperature<br>• Deposition efficiency |
| Other | • Torch assembly<br>• Electrode wear | | • Particle characteristics (size, shape, etc.) | • Substrate material |

# Equipment and Process Parameters



Plasma gas

High frequency starter

Heat Exchanger

Spray powder supply

Power supply

Gas and power control unit

Ar    He

Thermal Spray Fundamentals, Fauchais et al., 2014
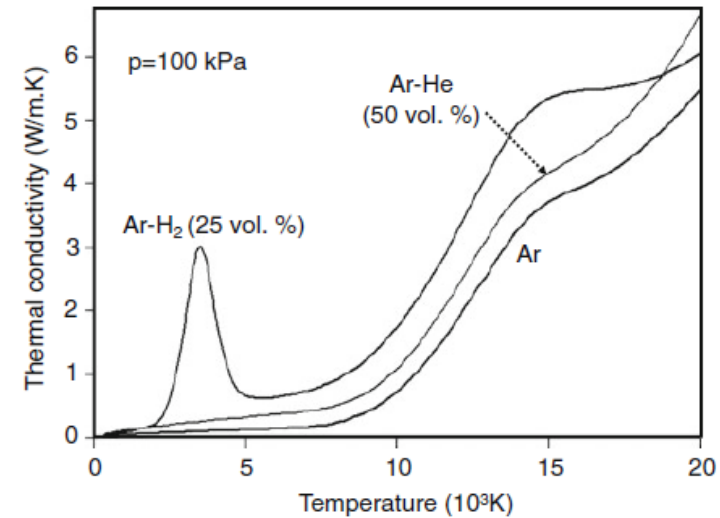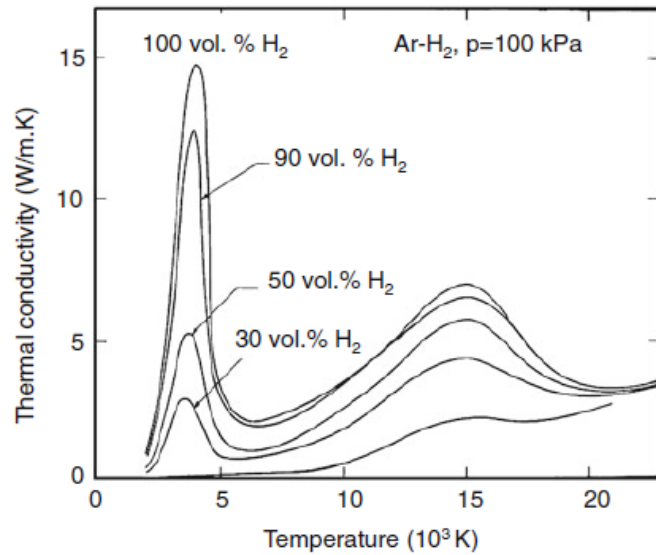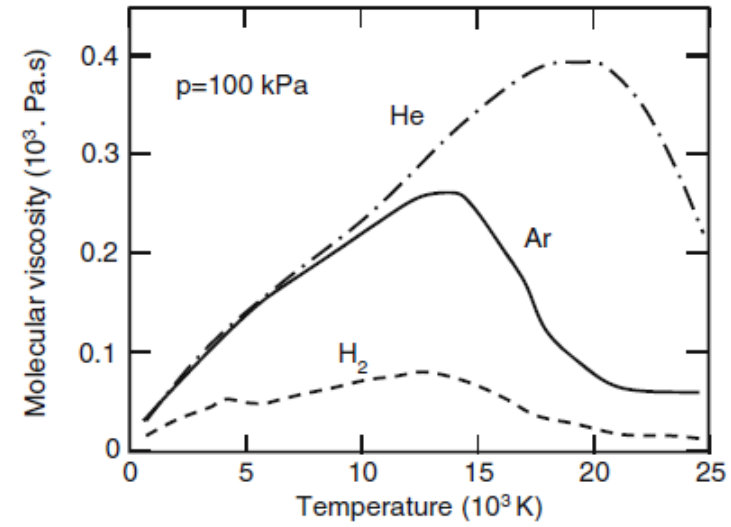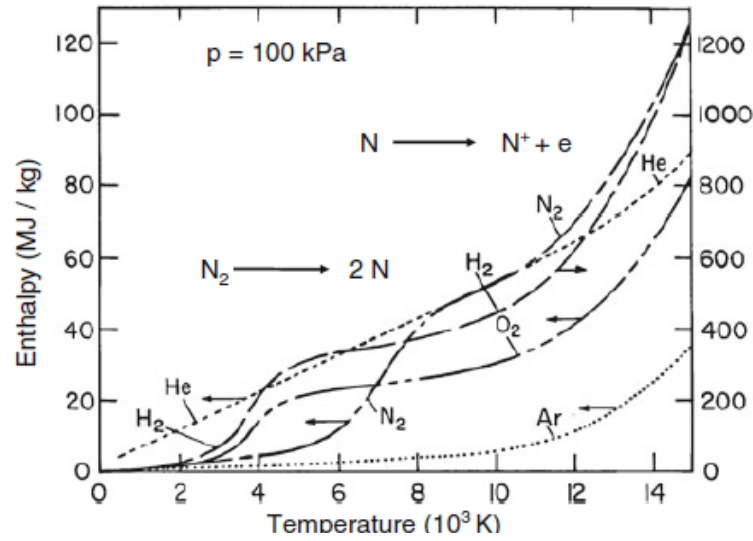
Images courtesy of NRC Canada

# Plasma Torch



- Integral energy balance (integrated over the radial coordinate):

$$\dot{m}\frac{\Delta \overline{h}}{\Delta z} + Q_{\text{cond}} + Q_{\text{Rad}} = I \times E$$

- Energy balance for the torch:
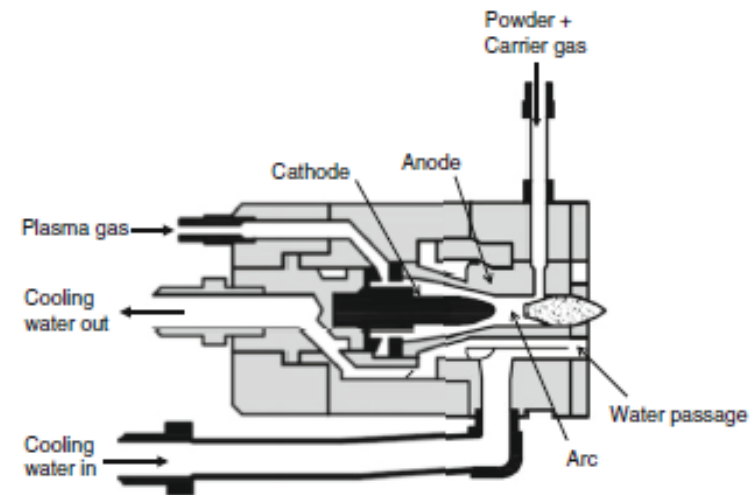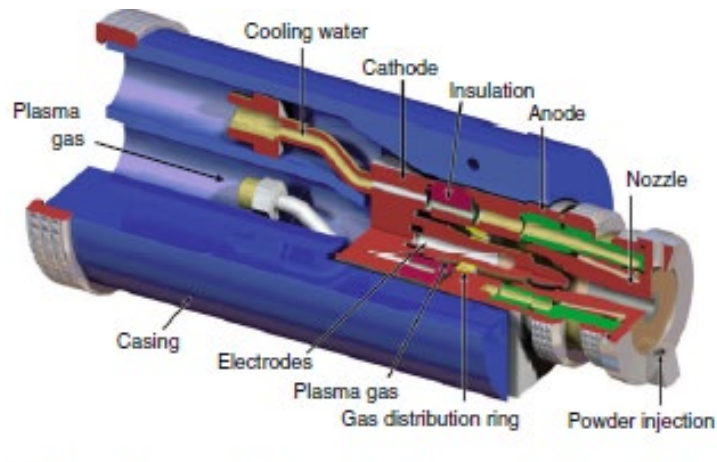
$$\dot{m}h_{\text{ave}} = \eta P_{\text{el}} = P_{\text{el}} - Q_{\text{Loss}}$$
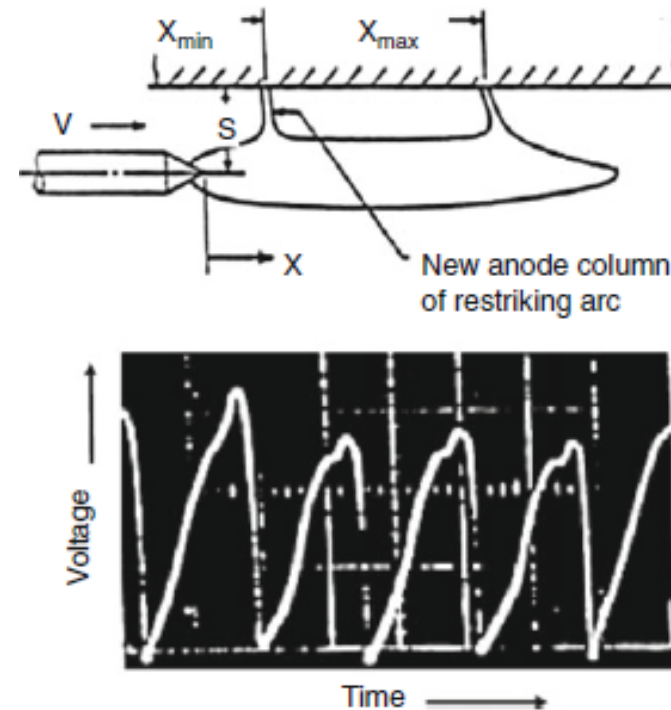
# Key Properties of Plasma Gases

# Plasma Torches

- Numerous different torches are available on the marketplace with different characteristics (power 15-200 kW, spray rate, size, radial or axial injection, etc.)

- 



Oerlikon Metco F4



Praxair SG100

Thermal Spray Fundamentals, Fauchais et al., 2014

# Plasma Jet Stability

- The arc root moves along the anode surface under the influence of:
  - drag force exerted by the cold flow in the boundary layer
  - Lorentz forces due the magnetic field induced by the curvature of the current flow.
- The voltage (and power) changes with the length of the arc
- Arc fluctuation frequency typically observed between 2-5 kHz



Thermal Spray Fundamentals, Fauchais et al., 2014

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# Plasma-particle Interaction

- The plasma fluctuations induced variations in the temperature and velocity of the spray particles
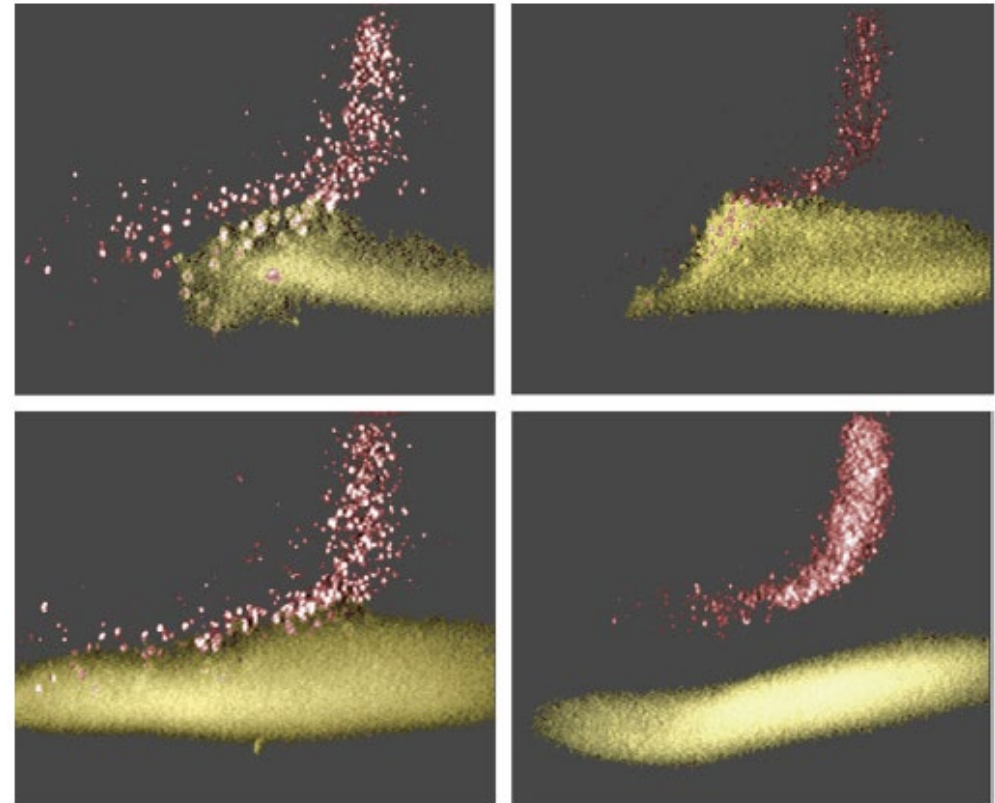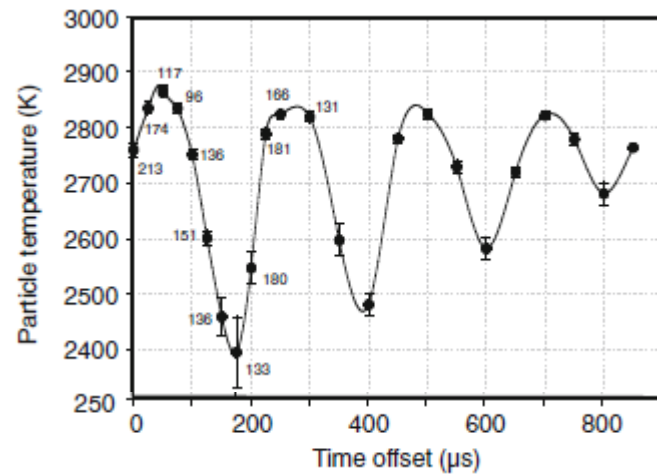




JF Bisson et al., J Therm. Spray Technol., 12 (2003)38–43

P. Fauchais, Understanding plasma spraying. J Phys D Appl Phys 37 (2004) 86–108

# Recent Developments

- More stable plasma torches typically operating at lower current and higher voltage:
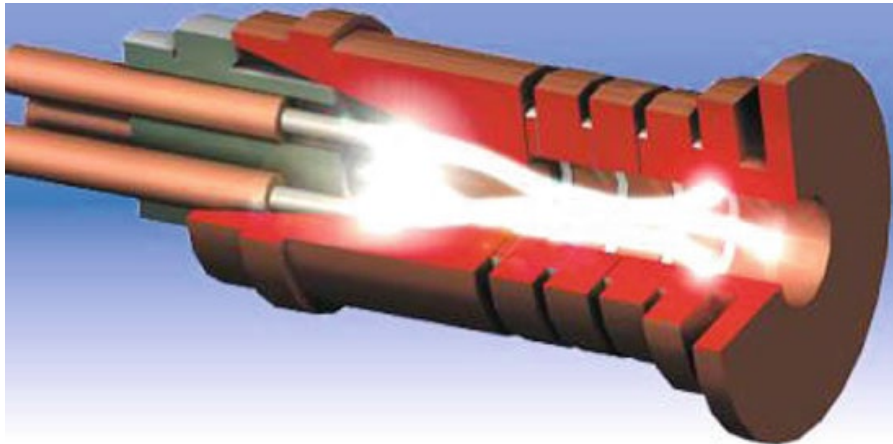  - Cascaded torch
  - Current is carried through 3 separate arcs

Triplex, Oerlikon Metco

Axial III, Mettech Corp.
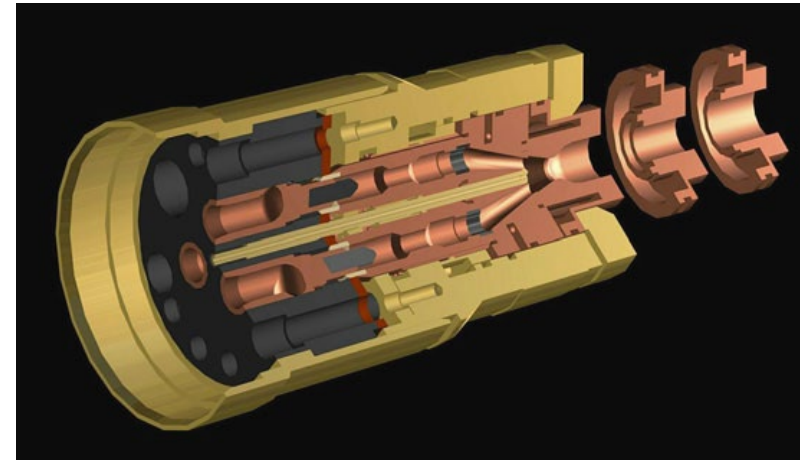




Thermal Spray Fundamentals, Fauchais et al., 2014

# Average Plasma Characteristics Downstream the Torch Exit
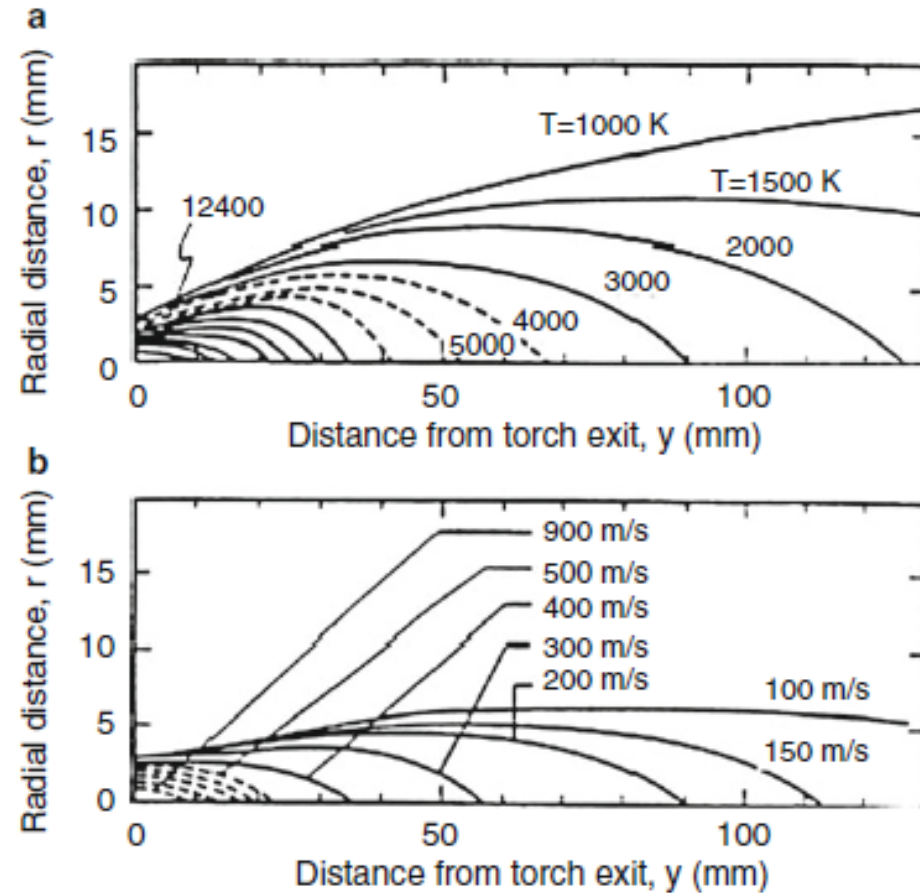


**Fig. 7.21** Temperature and velocity contours in d.c. plasma spray jet operated with nitrogen–hydrogen mixture [76] (with kind permission from Springer Science+Business Media B.V.)

# Turbulent Plasma Flow
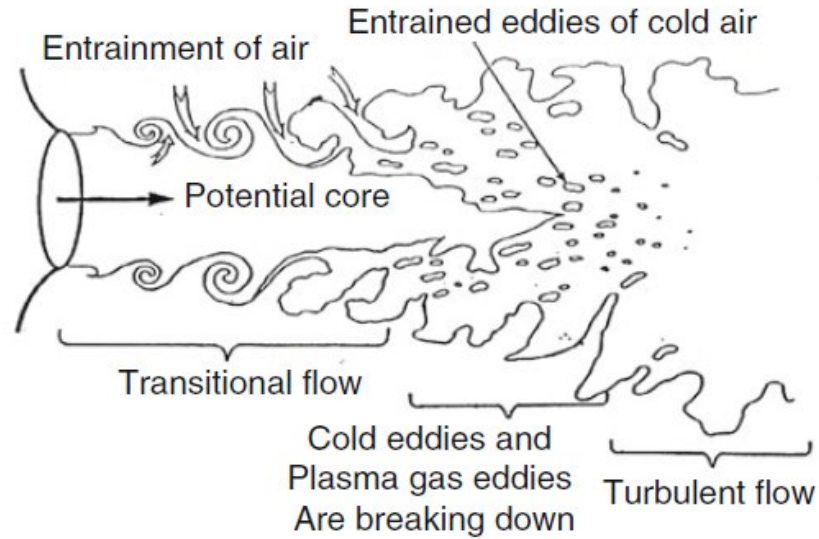


**Fig. 7.37** Schematic of the large-scale turbulence and cold gas entrainment in a plasma jet issuing into a cold gas environment and Schlieren images of a turbulent plasma jet [92]. Reprinted with permission of ASM International. All rights reserved
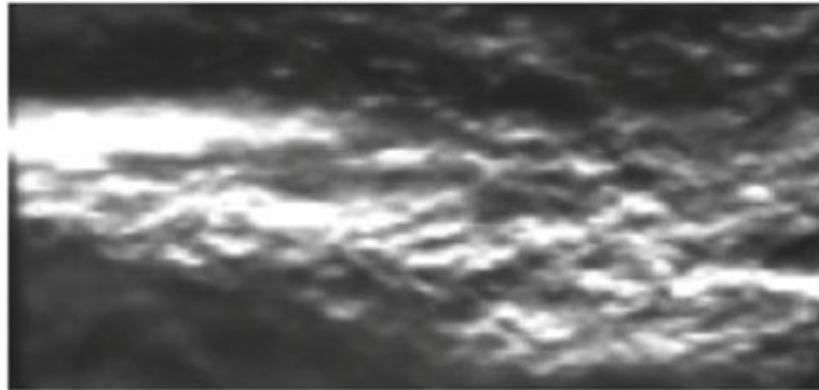
# Powder Injection and Trajectories

Fig. 2.18 Envelope of trajectories of particles injected radially for two powder size distributions (with one larger than the other) with the same mean size and same optimum trajectory

Particles:
— mean trajectory
- - - - narrow size distribution
- - - - wide size distribution

Injector

Torch

Energetic jet

Substrate
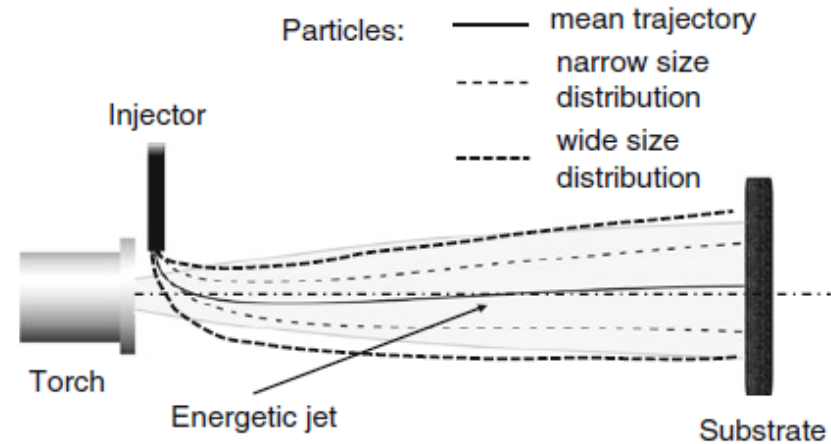
- Forces: inertia, drag (gravity negligible)

$$F_i = \frac{\pi d_p^3}{6} \cdot \rho_p \cdot \frac{du_p}{dt}$$

$$F_D = \frac{\pi d_p^2}{4} \cdot C_D \cdot \frac{1}{2}\rho \cdot u_R^2$$

# Heat Transfer

$$Q = h\left(\pi d_p^2\right)(T_\infty - T_s) - \left(\pi d_p^2\right)\varepsilon\sigma_s\left(T_s^4 - T_a^4\right)$$
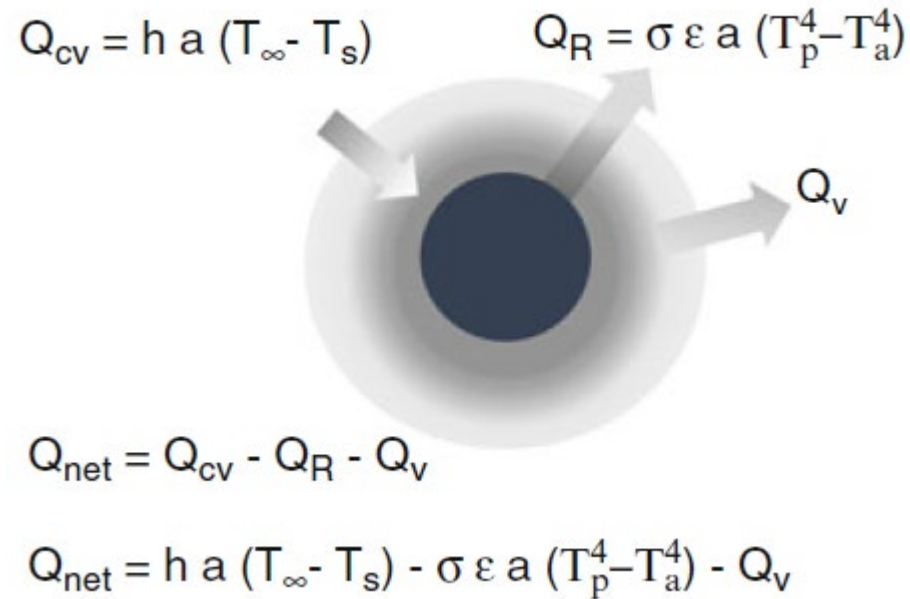
$$Q_{cv} = h\,a\,(T_\infty - T_s)$$

$$Q_R = \sigma\,\varepsilon\,a\,(T_p^4 - T_a^4)$$

**Fig. 4.20** Schematic of the net heat transfer to a particle, $q_{net}$ , where, $q_R$ radiative loss from the surface of a solid particle and $q_v$, heat loss from radiating vapor

$$Q_v$$

$$Q_{net} = Q_{cv} - Q_R - Q_v$$

$$Q_{net} = h\,a\,(T_\infty - T_s) - \sigma\,\varepsilon\,a\,(T_p^4 - T_a^4) - Q_v$$
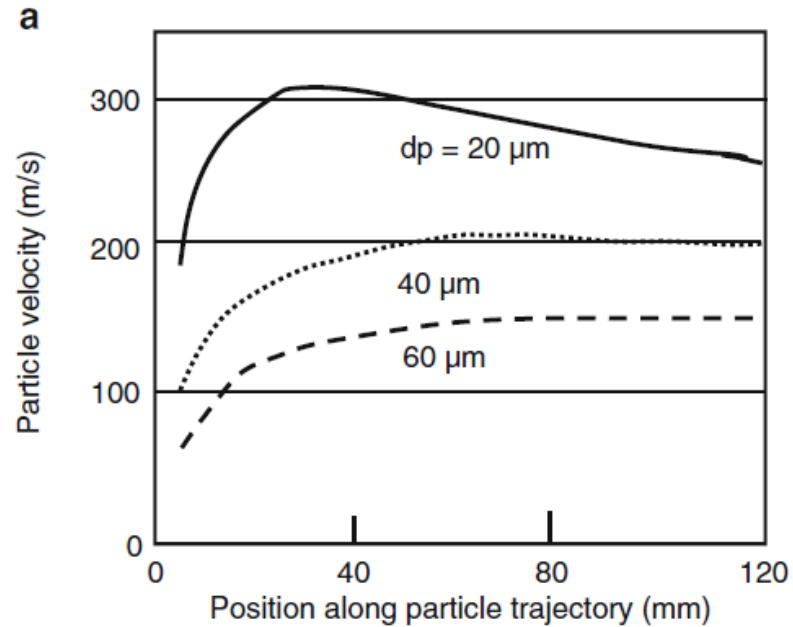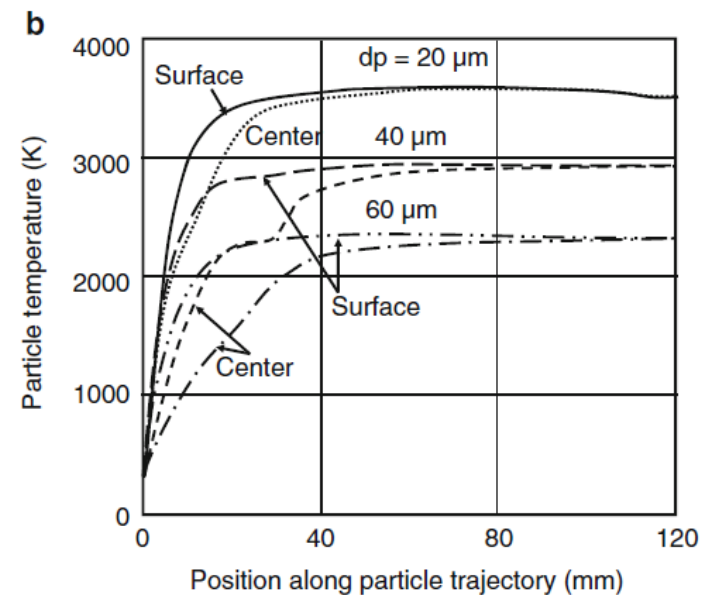
25

# In-flight Particle Characteristics



Fig. 4.38 Computed particle velocity (a) and temperature history (b) for dense Zirconia particles injected into an Ar–H$_2$ DC plasma jet: nozzle i.d. 6 mm, 35 slm Ar, 12 slm H$_2$, $I = 600$ A, $P = 35$ kW, $\eta_{th} = 55$ % [87]

# Feedstock - Powders

- Powder characteristics must be controlled tightly as they influence the particle injection and trajectories in the plasma and the resulting coating characteristics:
  - Particle size distribution
  - Particle shape
  - No segregation
  - Low humidity
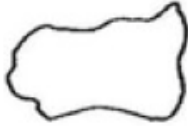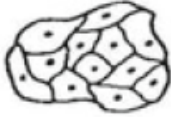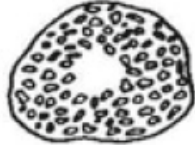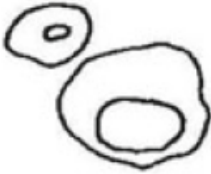  - Etc.

# Powder Characteristics

| Powder type Manufacturer | Fused and milled | Sintered and milled | Agglomerated and sintered | Spheroidized | Atomized |
|---|---|---|---|---|---|
| | | | | | |
| **Particle shape** | Blocky - angular | Blocky - angular | Spherical | Spherical | Spherical -irregular |
| **Porosity** | Dense | Dense - porous | Porous | Dense - hollow | Porous - hollow |
| **Crystalline size** | Course- fine | Course - fine | Medium - fine | Medium - fine | Fine |
| **Homogeneity** | Alloyed | Alloyed | Alloyed - heterogeneous | Alloyed - heterogeneous | Alloyed |

**Fig. 11.39** Specific $ZrO_2$–8 wt% $Y_2O_3$ powder characteristics depending on their manufacturing route. Reprinted with kind permission from Elsevier [47]

# Surface Preparation

- Adhesion mostly mechanical

- Majority of coating failures due to poor surface preparation
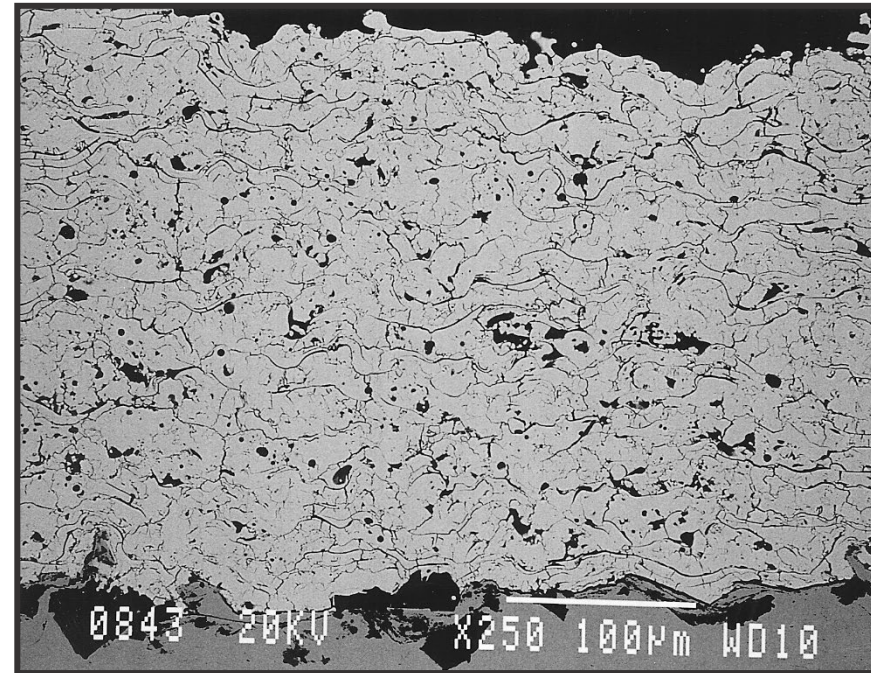
- Grit blasting
  - 36 to 60 grit Al2O3
  - Sand blasting is NOT acceptable

- Water Jet
- Laser cleaning



Progressive Technologies

# Plasma-sprayed Ceramic Coatings

Thermal Barrier Coating: Yttria partially stabilized
zirconia
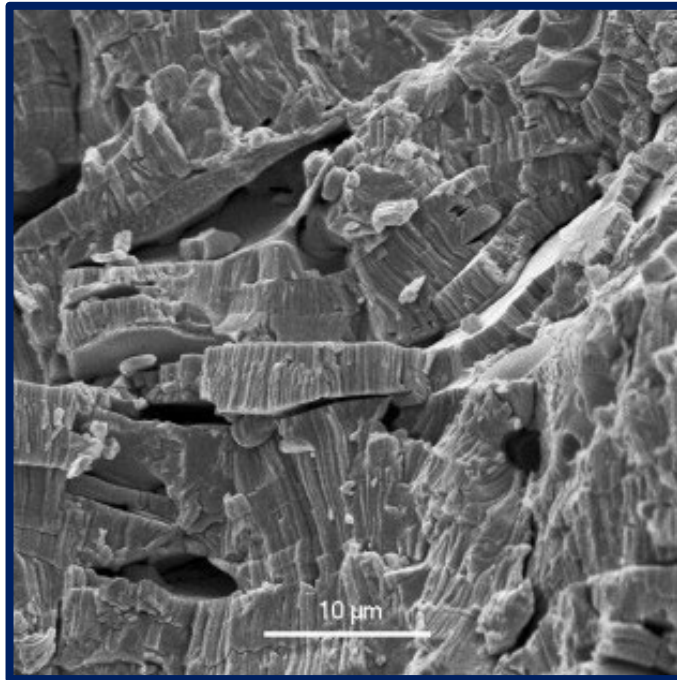


Clyne et al., Acta Metal., 2008

# Effect of Substrate Temperature

**25°C**　　　　**400°C**
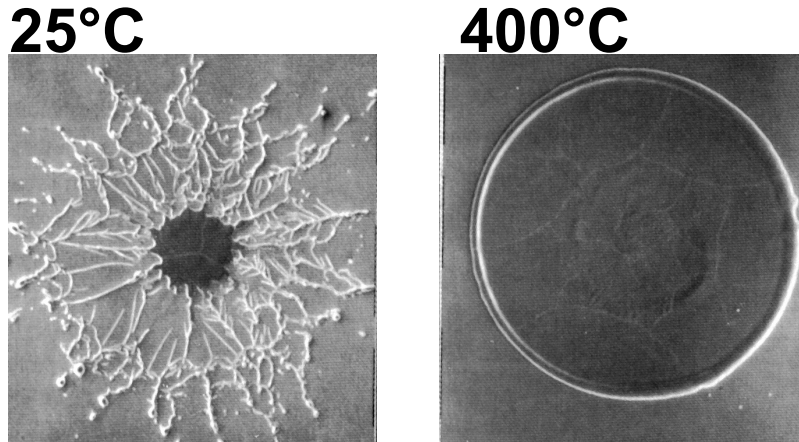


**after Fukomoto *et al.*, Proc. Int. Thermal Spray Conf., Kobe, 1995, p.353-8**



$$Velocity = \sqrt{\frac{Elastic\ modulus}{Density}}$$



**Substrate Temperature (°C)**
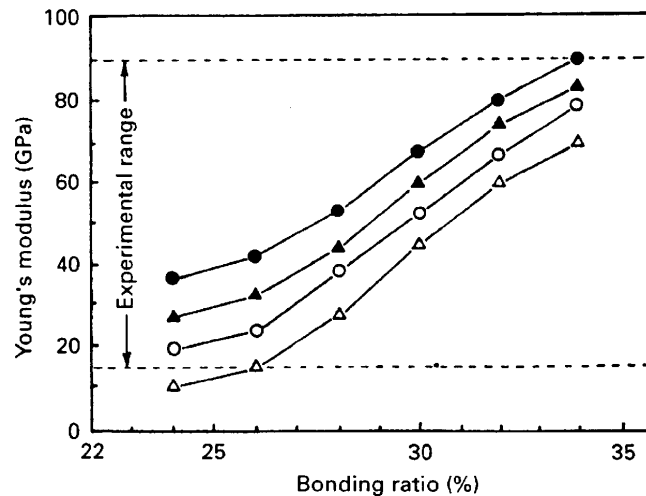
after C.J. Li et al., J. Mat. Science 32 (1997) 997
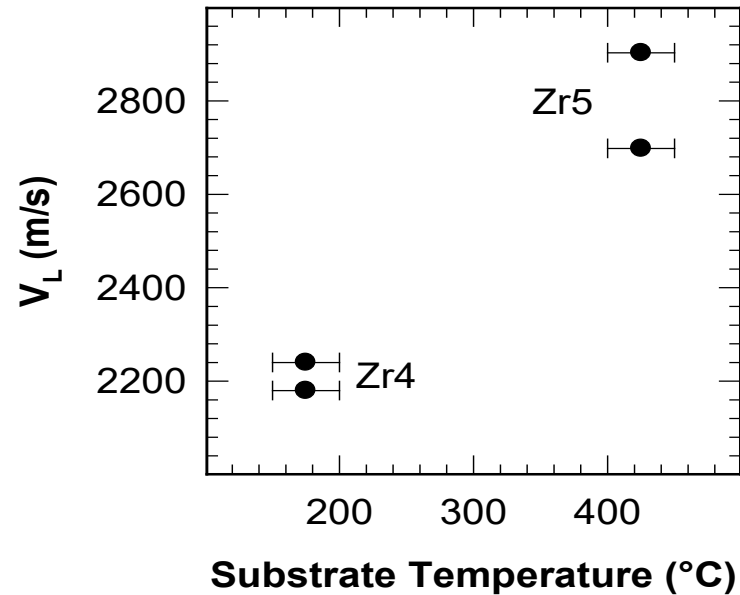
# W Coating Structure – Cu infiltrated
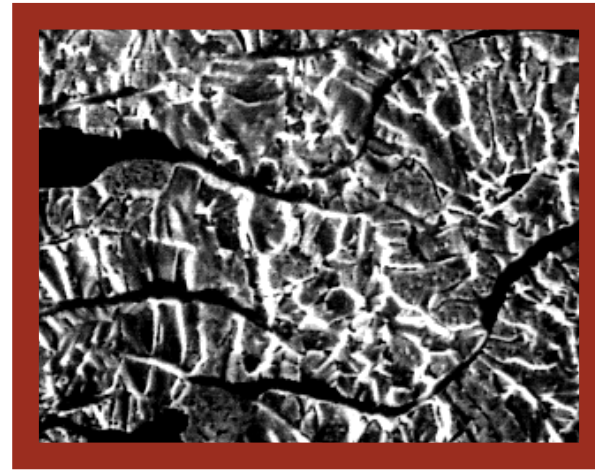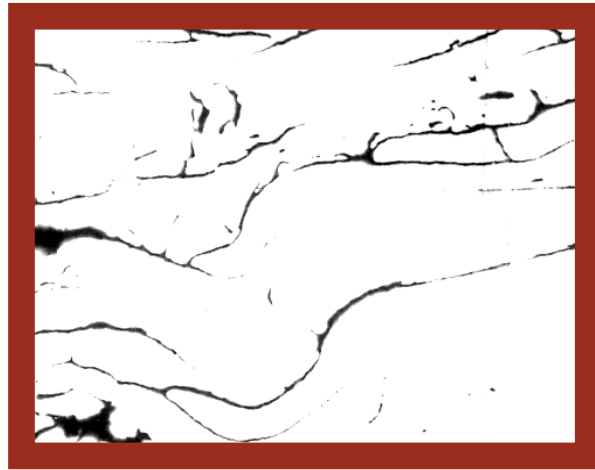


**20 µm**

**Polished**

**Etched**

S. Boire-Lavigne et al., J Therm. Spray Technol., 4 (1995) 261-267

# Thermal Conductivity of W Coatings
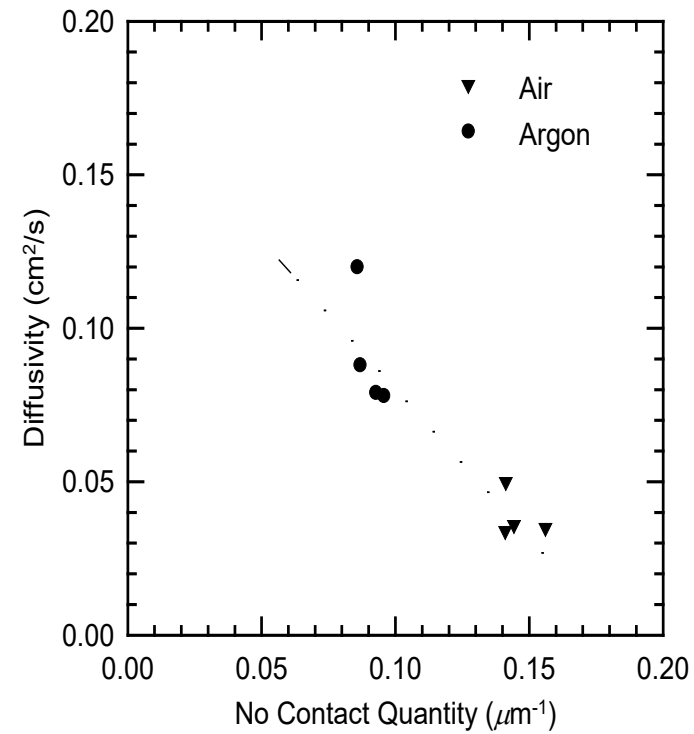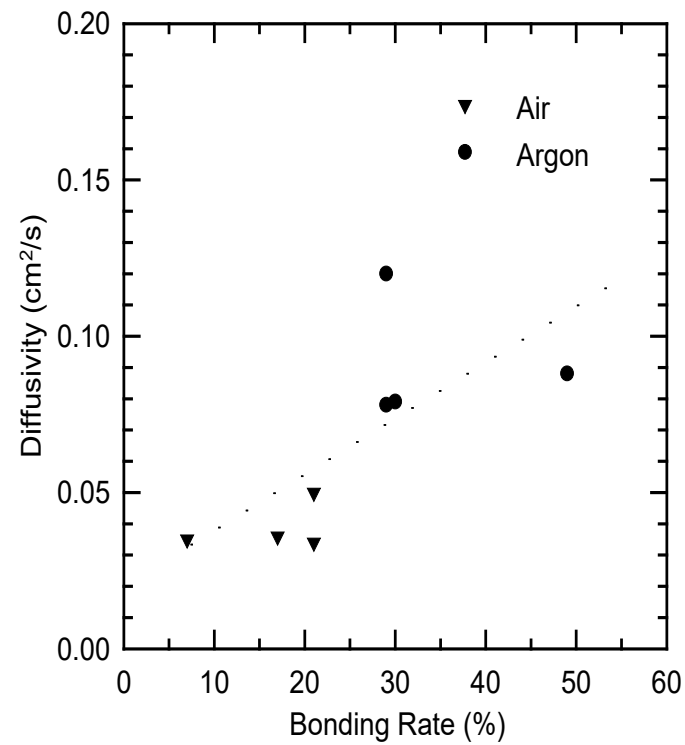


S. Boire-Lavigne et al., J Therm. Spray Technol., 4 (1995) 261-267

# Lamellar Structure



Coating

Interlamellar Void

$2r$

$\delta$

True Contact

A - - - - - - - - - - - - - - - - - - - - - - A

Substrate

Section AA

Interlamellar Void

True Contact

True Contact

Oxide Film

Interlamellar Void

Heat Flux
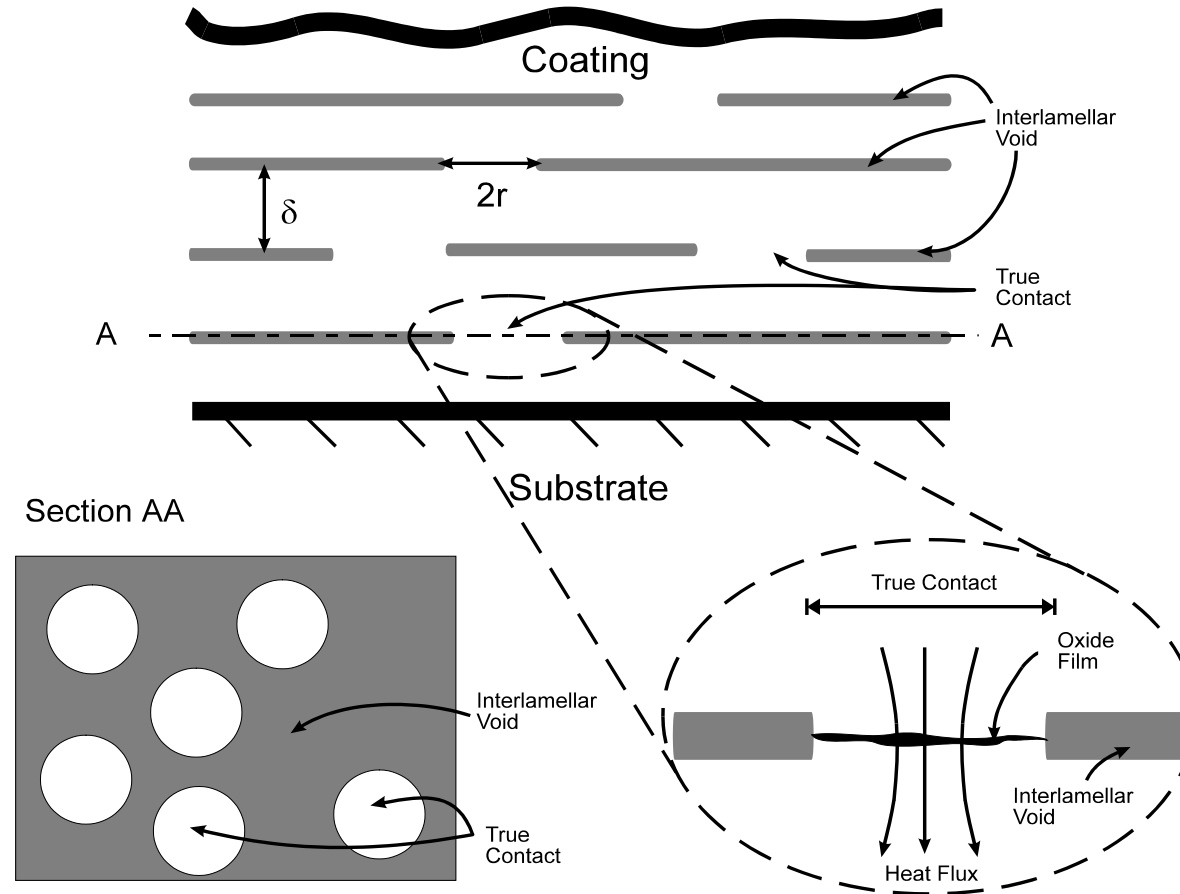
S. Boire-Lavigne et al., J Therm. Spray Technol., 4 (1995) 261-267

# Nanostructured YSZ TBCs

- Nanostructured porous powders and coatings
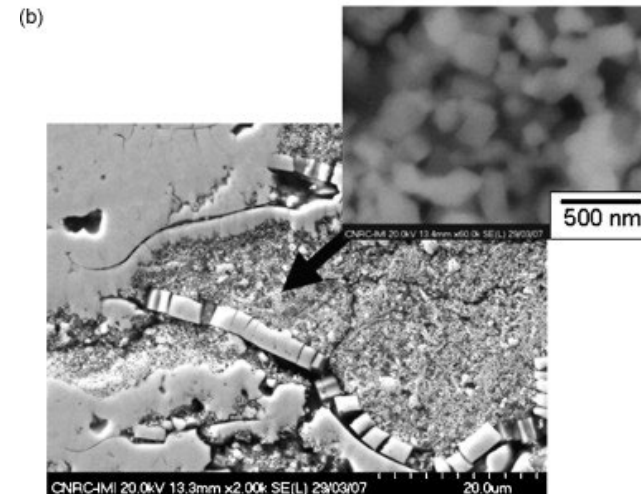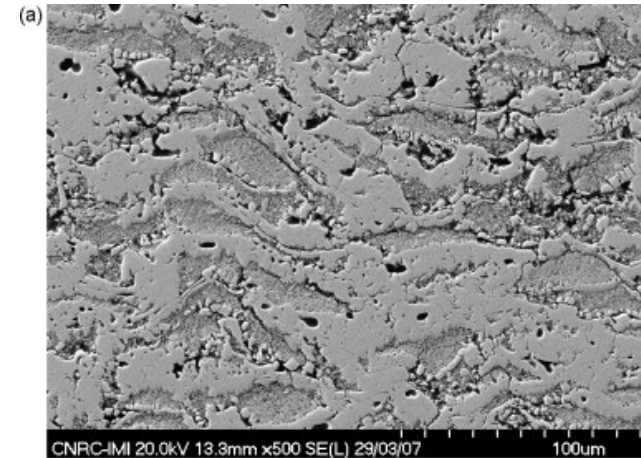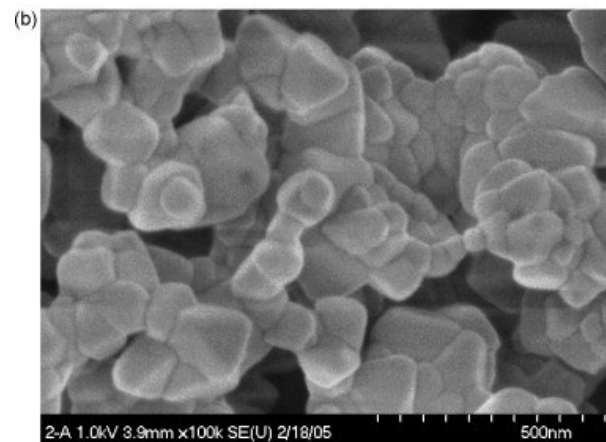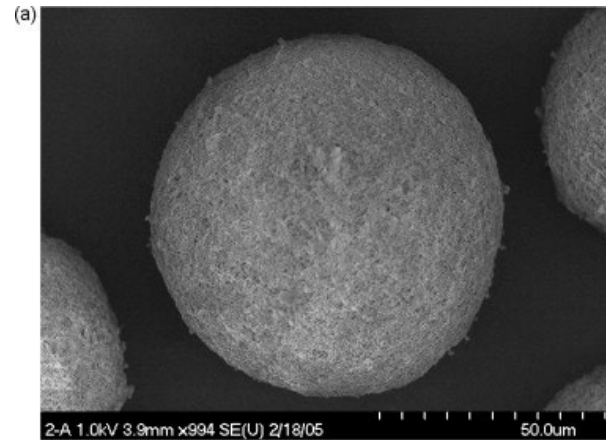


R. Lima and B. Marple, Mat. Sci. & Eng. A, 485
(2008) p. 182-193

# Nanostructured YSZ TBCs

- Lower thermal diffusivity
- Lower elastic modulus
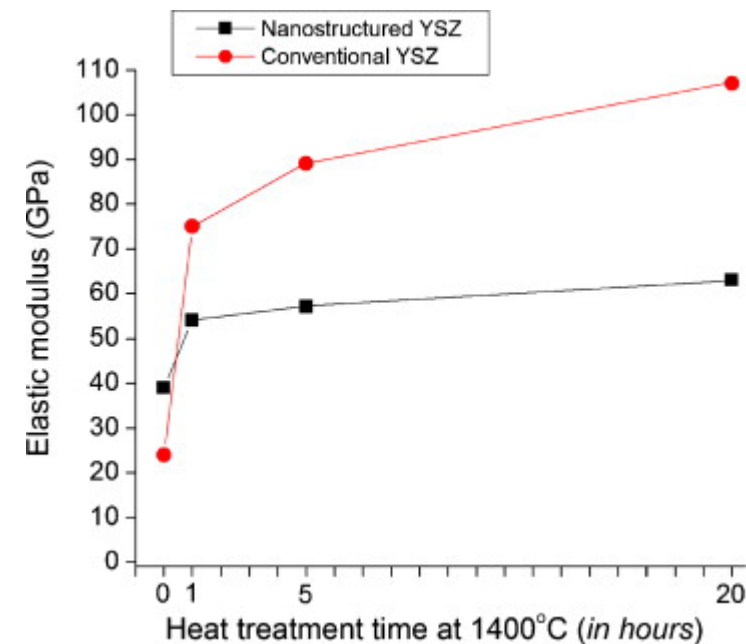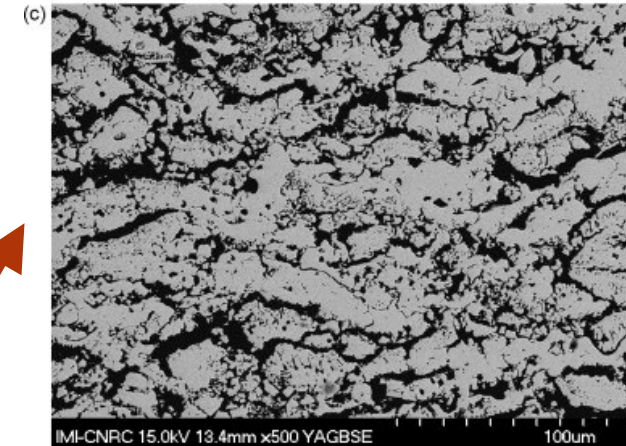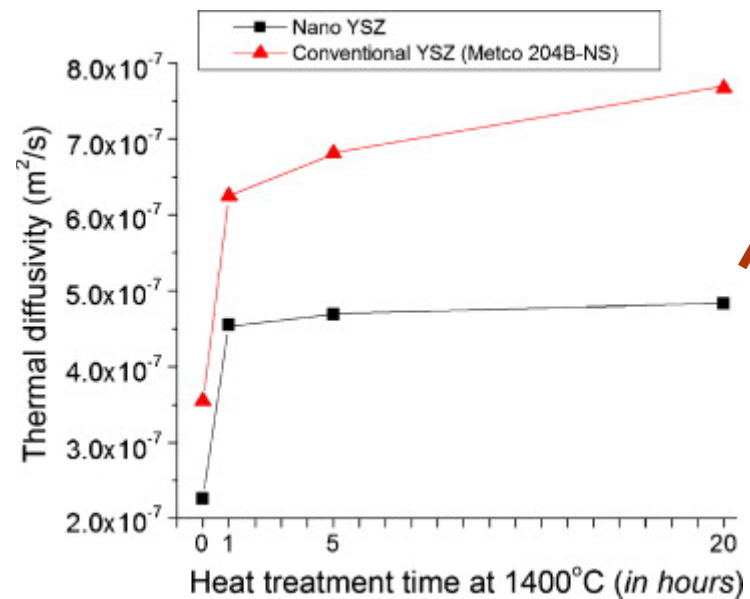


R. Lima and B. Marple, Mat. Sci. & Eng. A, 485 (2008) p. 182-193

# Substrate and Coating Temperature

- Influence on:
  - interface quality between lamellae
  - residual stresses
  - crack formation
  - thermal conductivity
  - elastic modulus, etc.

- Measuring techniques:
  - one- or two-color pyrometer
  - infrared camera
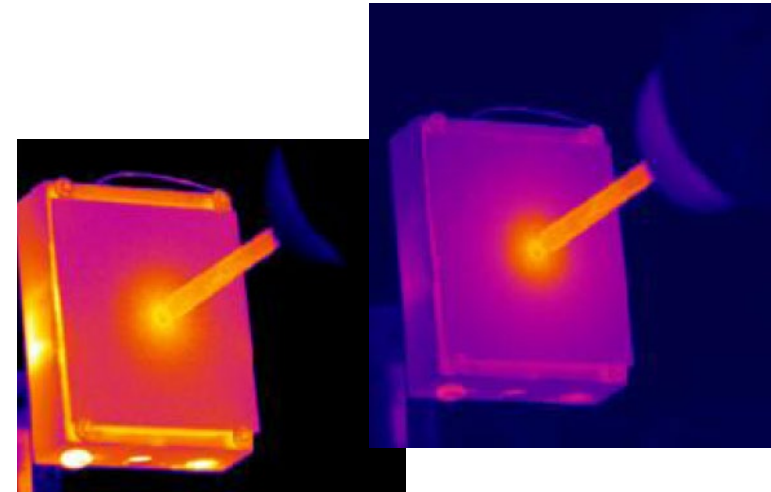
Images courtesy of NRC Canada

# Spray Booth



Oerlikon Metco : http://www.oerlikon.com/metco/en/products-services/coating-equipment/thermal-spray/systems/plasma/
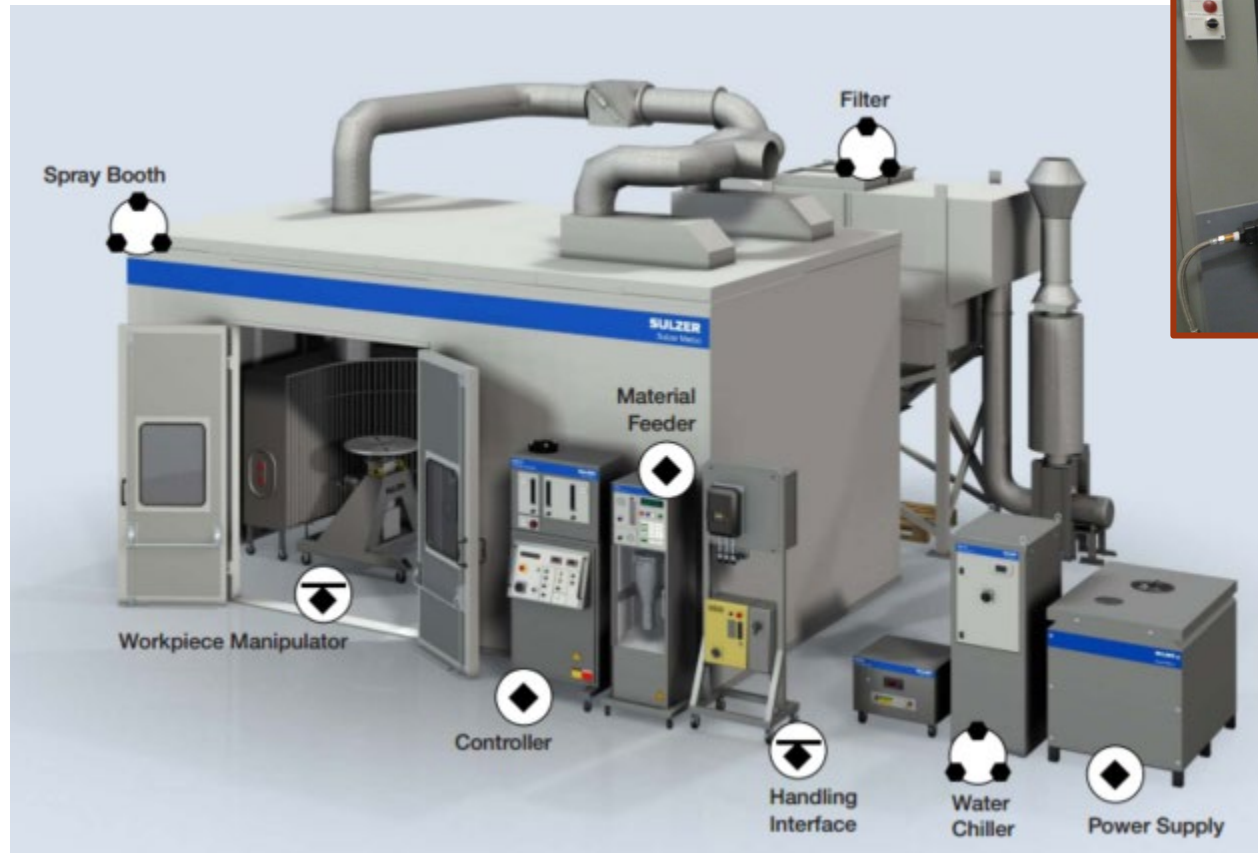
# Safety Consideration

- Safety issues:

  - Noise

  - UV light

  - Dust and fumes

  - Heat

  - Robot

  - Electrical shocks

## Measures:

- Adequate thermal spray booth design

- Personal protection

- Adequate gas and fuel handling infrastructure

- Adequate operation practices

More at: http://tss.asminternational.org/portal/site/tss/SafetyGuidelines/

# Suspension Thermal Spraying

- Fine droplets formed by injection of submicron powders (STS) in the flame
- Cooling rates exceeding 10 million °C/sec → formation of nanograins



Grain size range (20-80nm)
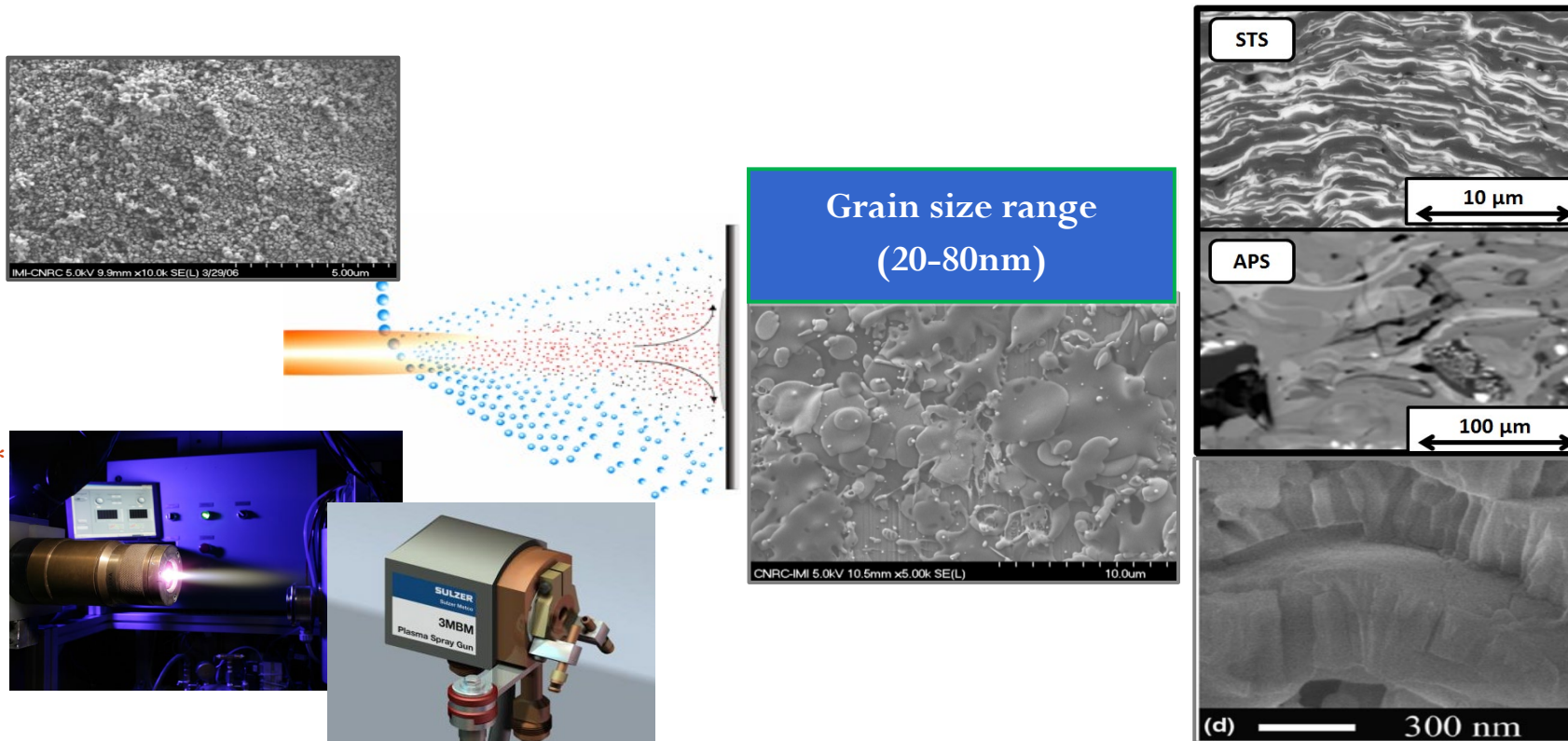
*Image courtesy of NRC Canada

VanEvery et al., JTST, Vol. 20 (2011) p. 817

# Suspension/Jet Interaction

- Complex phenomena occur sequentially:
- Primary and secondary atomization
- Liquid evaporation
- Sintering and melting of the spray material



Aerodynamic breadown | Evaporation of liquid | Sintering of some fine solids | Melting of fine solids and agglomerates | Evaporation from melt | Impact
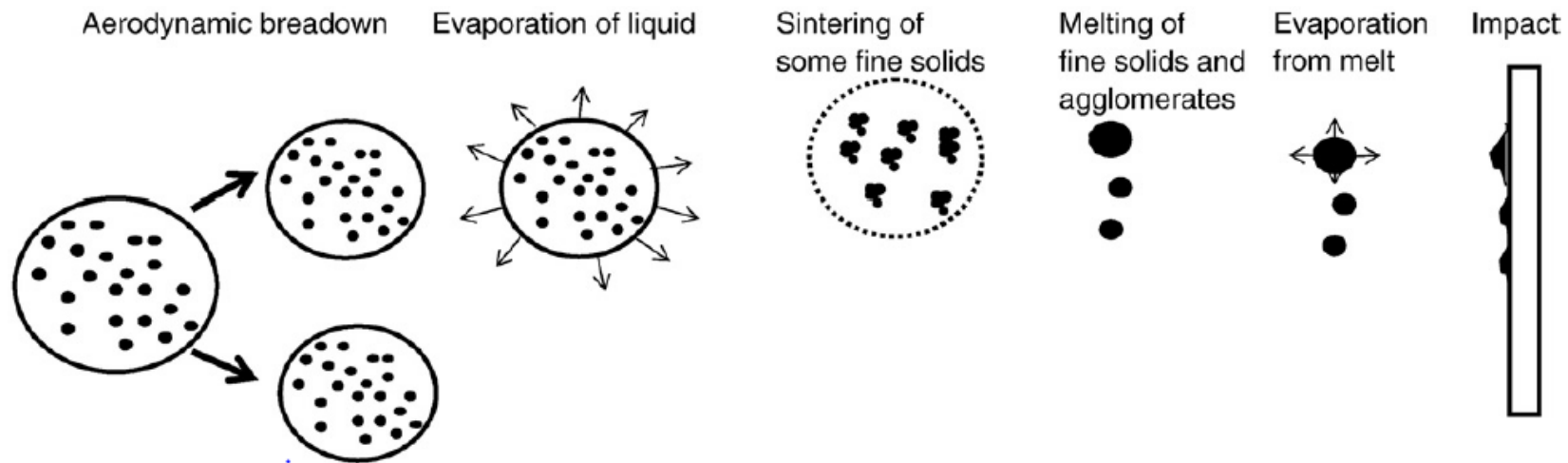
L. Pawlowski, Surface and Coating Technol. 203 (2009) 2807-2829

# Modelling and Simulation

- Atomization behaviour of multiphase fluids containing nanoparticles. Nanoparticle/ fluid thermal interaction
- Determination of in-flight particle characteristics by numerical modelling
- Multiscale modeling of nanomaterials properties

Liquid jet in cross flow
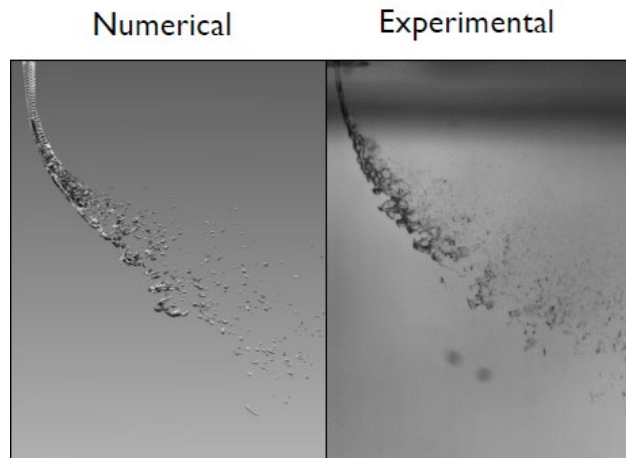
Modeling of an effervescent atomizer



Numerical        Experimental

V (m/s)

SPS particle size and temperature at 9 cm stand off

# Reduced Particle Impact Velocity

➤ Critical to control the microstructure
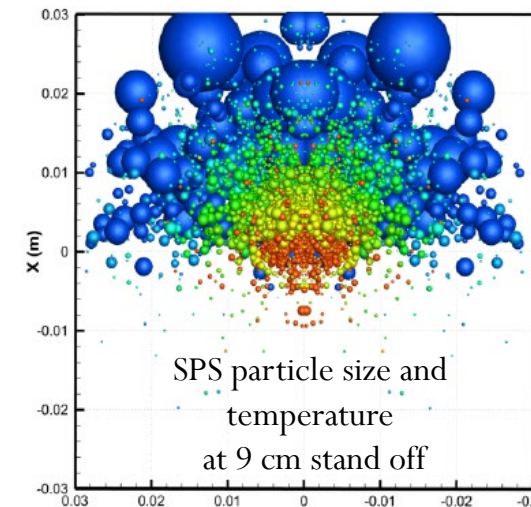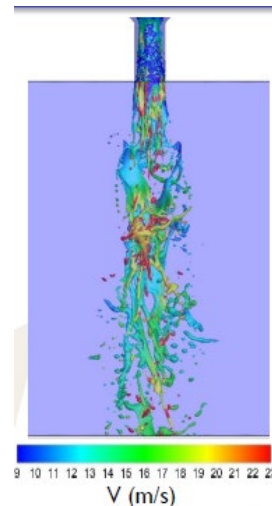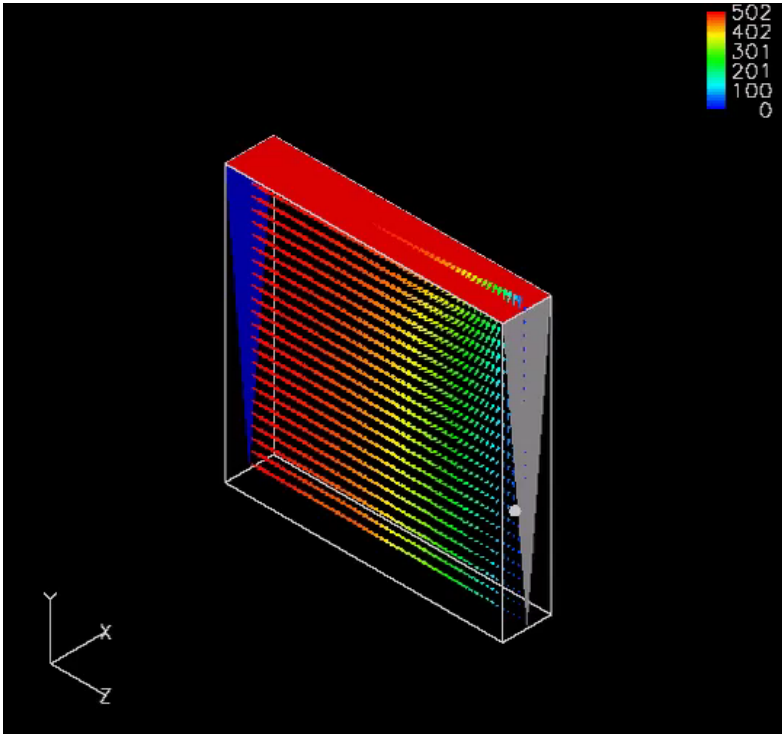
**Gas Flow Simulation with CFD 2000 Adaptive Research®**

**Particle Velocities**

Normal velocity (m/sec) vs. Distance above substrate (cm)

- 40 µm
- 5 µm
- 3 µm
- ZrO$_2$
- Al$_2$O$_3$
- 2 µm
- 1 µm
- Gas Velocity

ZrO$_2$ particles
Al$_2$O$_3$ particles

Isothermal 22% H$_2$ in Ar,
µ = 0.000128 kg/sec at 3300°C, 400 m/sec.
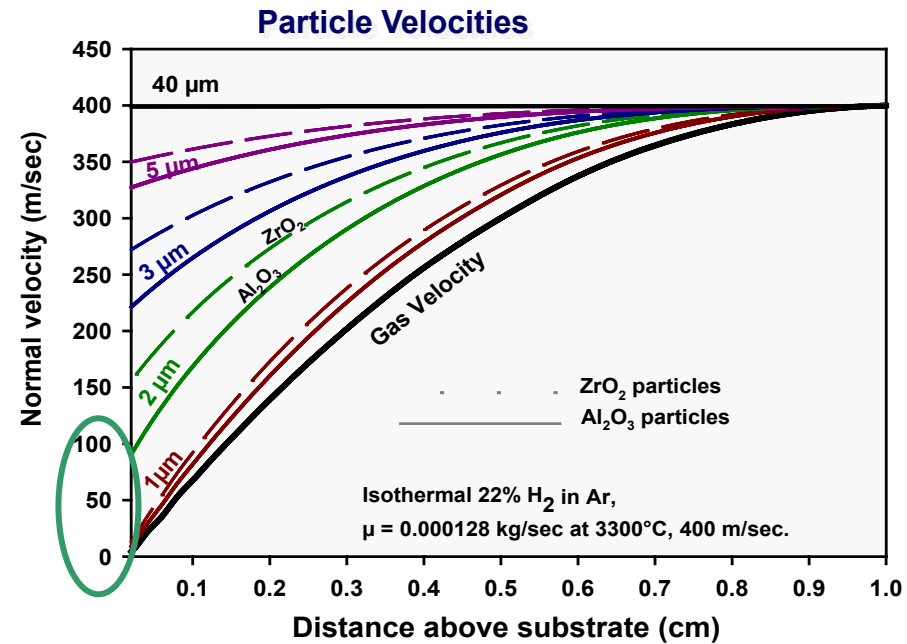
➤ **Highly sensitive to particle size and material density**

➤ **Higher free stream velocities can dramatically increase the impact velocity of small particles**

J. Oberste-Berghaus, et al., ITSC Proceedings 2005, Basel (Switzerland)

# Coating Build-up

- STS typical microstructure formation depends strongly on the particle velocity at impact:
  - Normal direction
  - Parallel direction
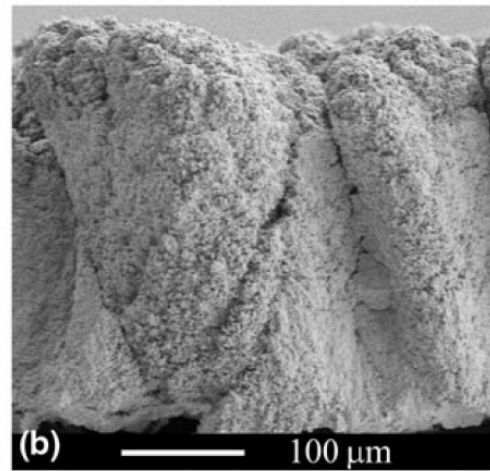


Deflection of the particle trajectory depends on the Stokes number *St*:

$$St = \frac{\rho_p d_p^2 v_p}{\mu_g l_{BL}}$$

P. Fauchais, et al., JTST, 17 (2008) 31-59
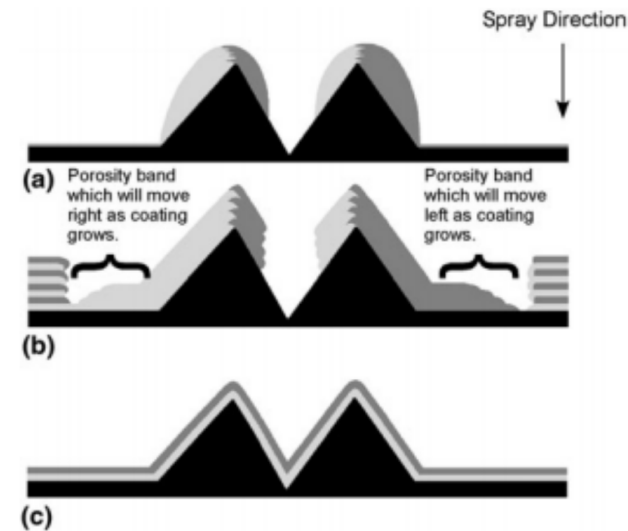


K. VanEvery, et al., JTST, 20 (2011) 817-828

# Controlling SPS Coating Structure

- A designed cooling system allows:
- driving out the low-velocity particles before their impact onto the substrate
- maintaining the nominal temperature of the substrate by playing on the cooling gas flow rate
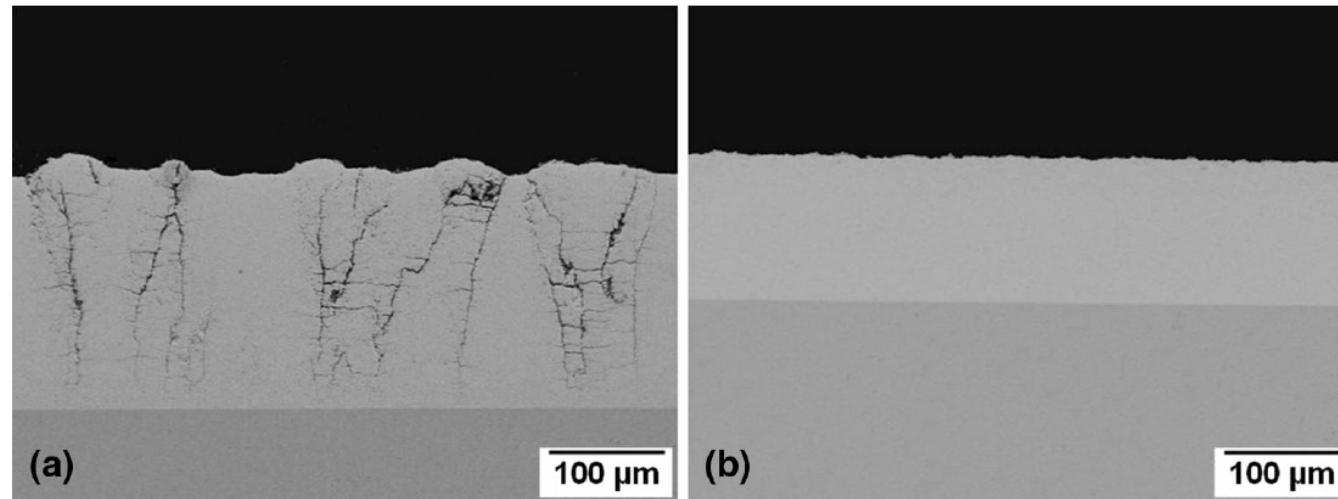


A. Joulia, et al., Published online 8 Nov. 2014

# Suspension Plasma Spraying for Thermal Barrier Coatings (TBCs)

- **Promising coating process:**
  - SPS coating structures comparable with EB-PVD coatings
  - Important potential cost savings

- After Z. Tang, H. Kim, I. Yaroslavski, G. Masindo, Z. Celler and D. Ellsworth, « **Novel Thermal Barrier Coatings Produced by Axial Suspension Plasma Spray** », ITSC 2011, Hamburg, Germany
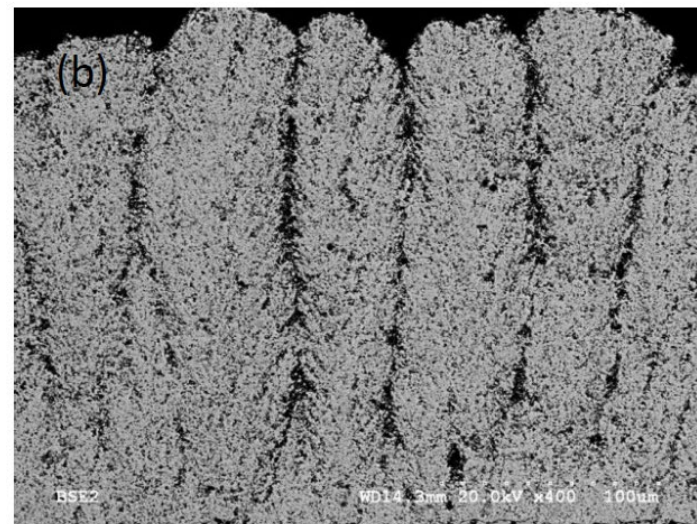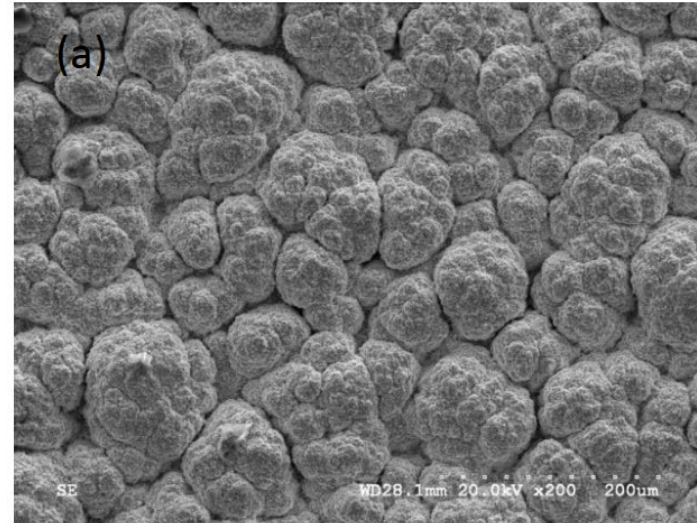
# Superhydrophobic Coatings for Reduction of Ice Accumulation



Aluminum

Difference in ice formation on a superhydrophobic and a aluminum surface in icing condition

Cold Air flow

Superhydrophobic

Ali Dolatabadi, 2010

APS Contact angle ≈ 145°

SPS Contact angle ≈ 167°
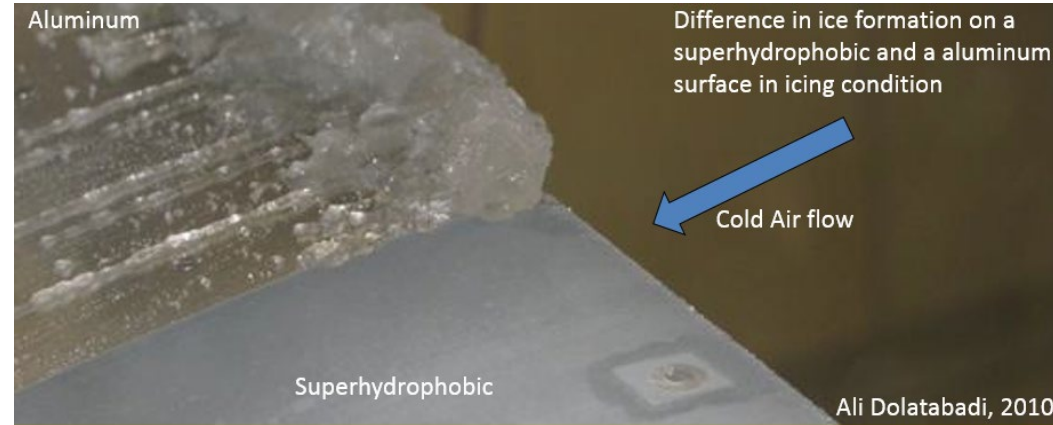
- APS and SPS $TiO_2$ coatings treated with stearic acid solution

TMG 15.0kV 10.1mm x500 SE          100um

TMG 15.0kV 10.0mm x500 SE          100um

N. Sharifi, at al., ITSC 2015, Long Beach (California)
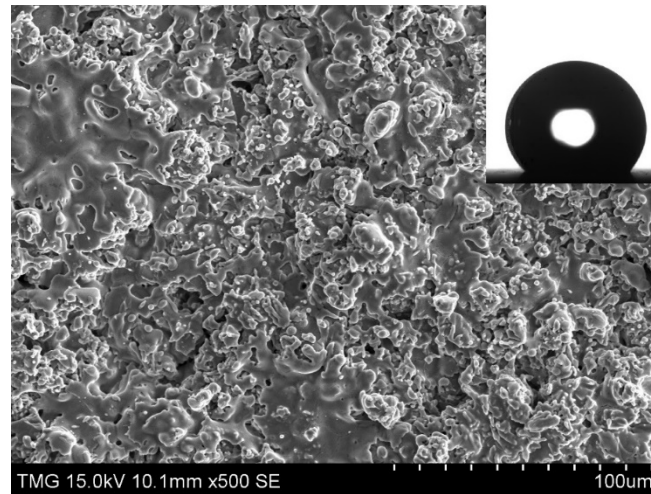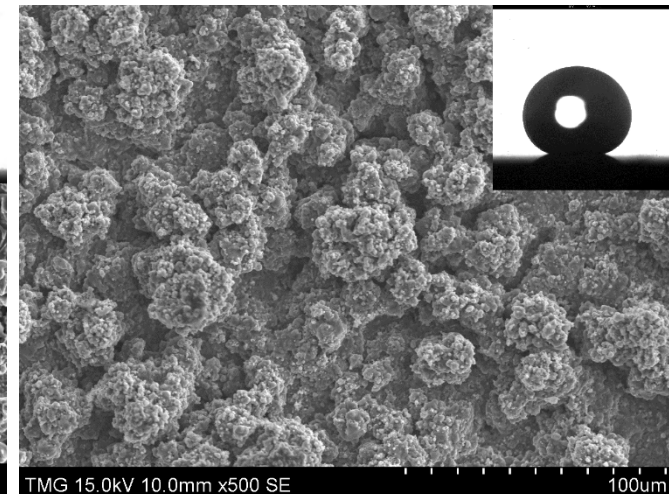
# Combustion Processes

# Combustion Temperature
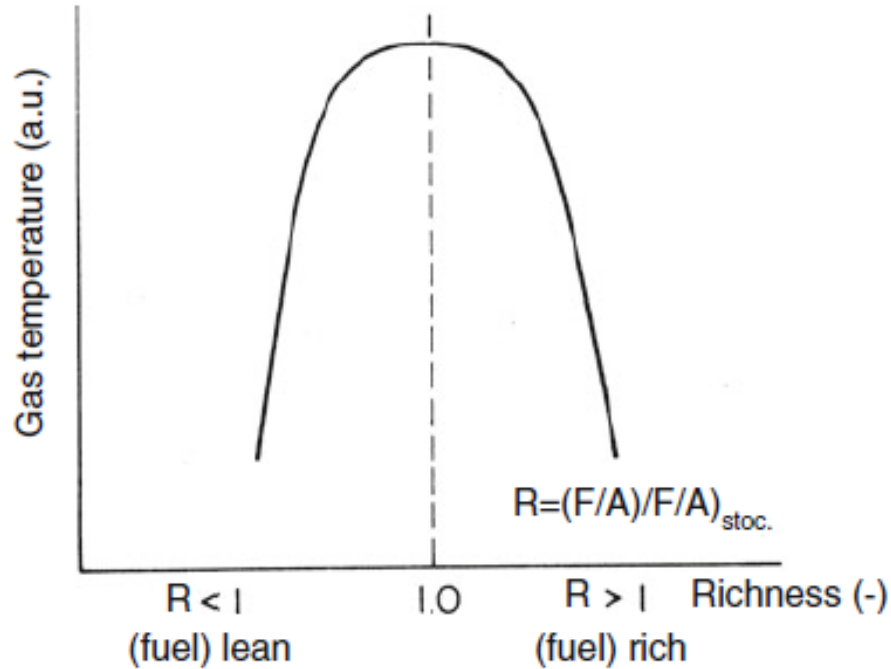


Fig. 3.1 Variation of combustion temperature with richness ratio [1], reprinted with the kind permission of Elsevier
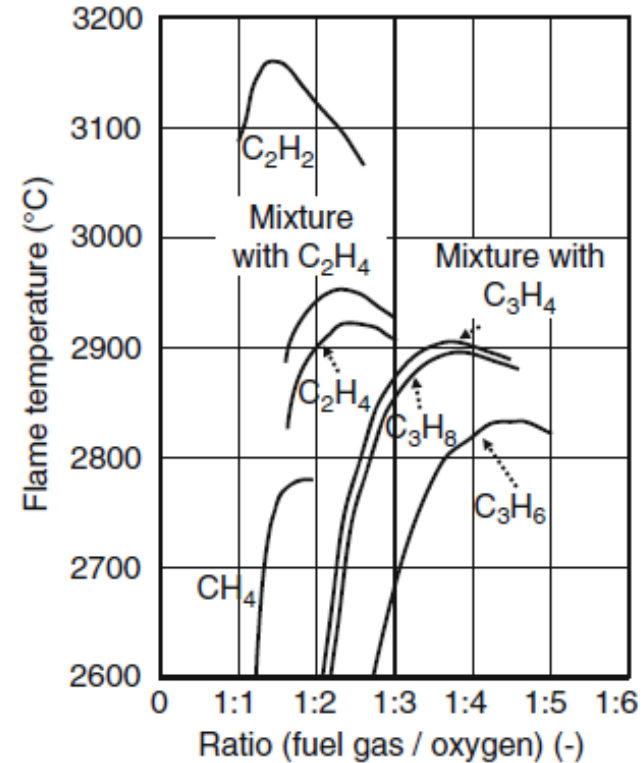


Fig. 3.2 Flame temperatures as function of the fuel/oxygen ratio for different mixtures fuel/oxygen by volumes ($m^3/m^3$) and for different hydrocarbon fuel gases [2], reprinted with the kind permission of Linde Co

# Combustion with Air and Oxygen

Table 3.1 Approximate flame temperatures of various stoichiometric mixtures (initial temperature 298 K, atmospheric pressure) [1], reprinted with the kind permission of Elsevier

| Fuel | Flame temperature (K) Air as oxidizer | Flame temperature (K) Oxygen as oxidizer |
|---|---|---|
| Acetylene | 2,600[a] | 3,410[b] |
| Carbon monoxide | 2,400 | 3,220 |
| Heptane | 2,290 | 3,100 |
| Hydrogen | 2,400 | 3,080 |
| Methane | 2,210 | 3,030 |

[a]This maximum exists at $R' = 1.3$
[b]This maximum exists at $R' = 1.7$

# Combustion: Spray Processes History

**Table 5.1** Major dates related to the development of the major thermal spray processes

| Year | Process | Energy generation | Inventor(s) | References |
|------|---------|-------------------|-------------|------------|
| 1909 | Flame spraying (FS) | Combustion (diffusive) | Schoop (Switzerland) | [1] |
| 1955 | Detonation gun spraying (D-Gun) | Combustion (detonation) | Gfeller and Baiker[a] (USA) | [2] |
| 1983 | Supersonic flame spraying (HVOF) | Combustion (deflagration) | Browning (USA) | [3] |

[a]Union Carbide, today Praxair Surface Technology (USA)

# Flame Spray: Powder and Wire
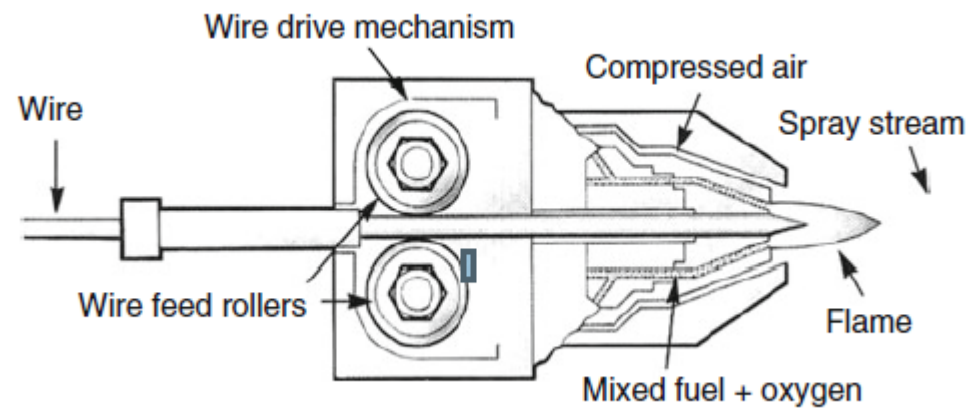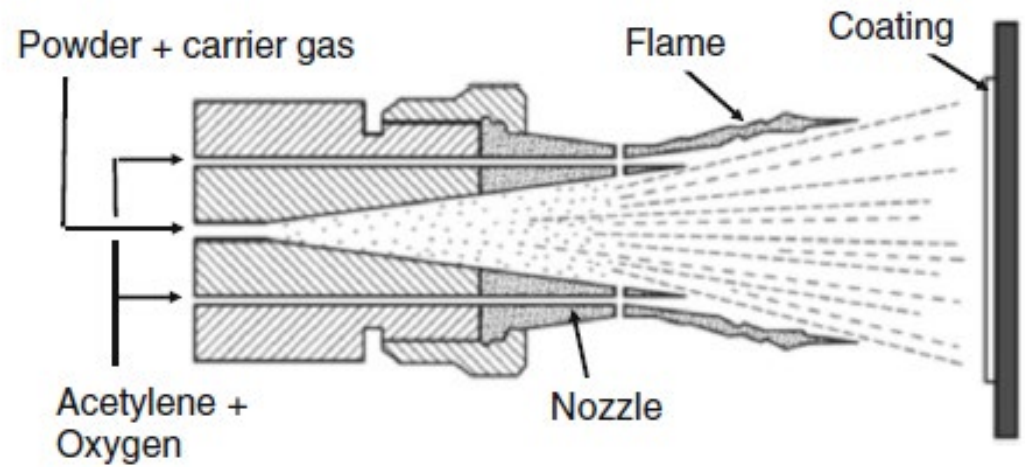
# Flame Spaying

- Particle characteristics
  - temperature ~ 300-3000°C
  - speed ~ 30-50 m/s
- Materials - polymers, metals and ceramics
  - spray rate ~ 2 to 3 kg/hour
- Coating characteristics
  - density ~ 5 to 15% porosity

# HVOF: Gas and Liquid Fueled
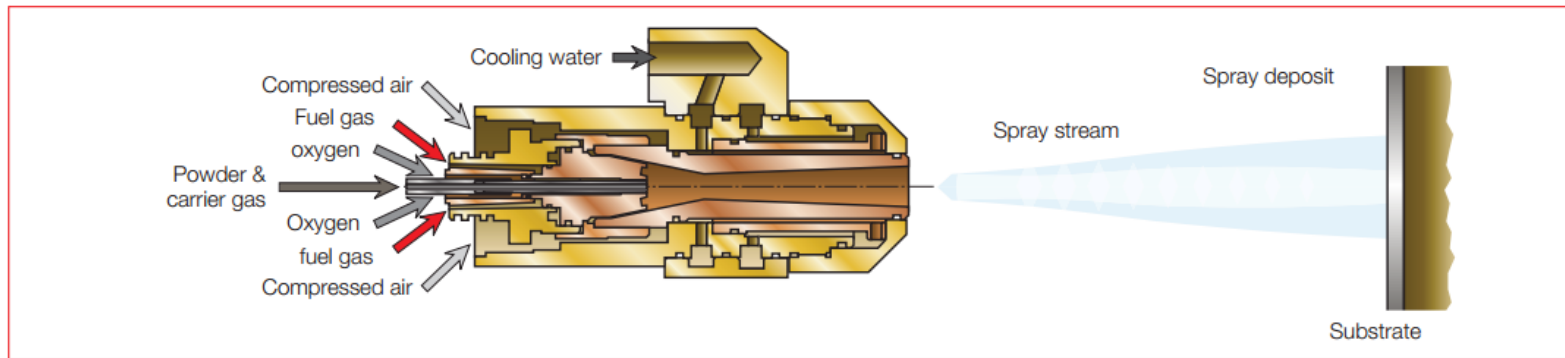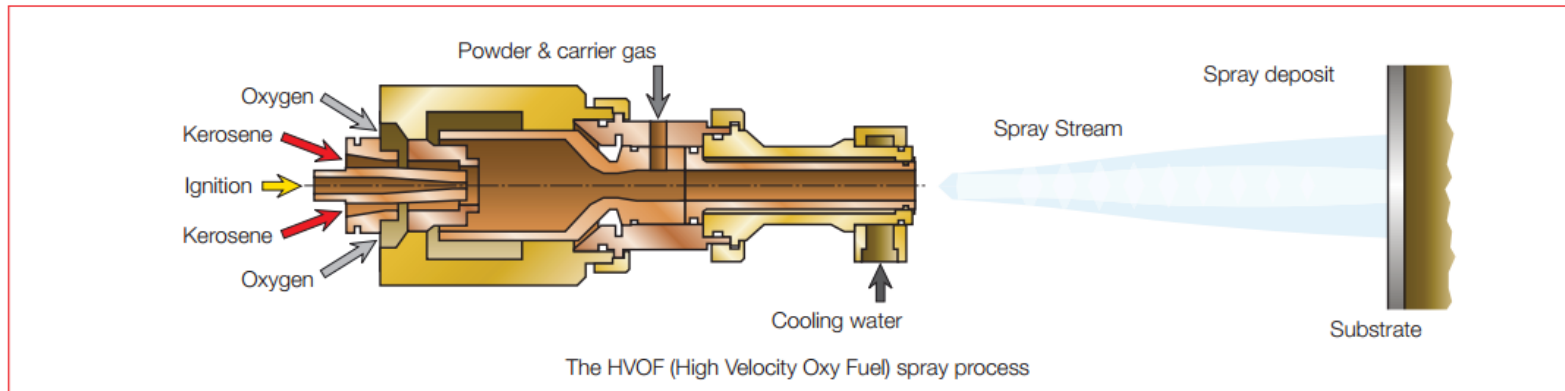


High Velocity Oxy-Fuel (HVOF) Solutions, Oerlikon Metco:
http://www.oerlikon.com/ecomaXL/files/metco/oerlikon_HVOFSolutions_EN6.pdf&download=1

# HVOF: Gas and Liquid Fueled

| Comparison | Gas fuel HVOF | Liquid fuel HVOF |
|---|---|---|
| Gun | Water-cooled Diamond Jet Gun | WokaJet™-410-Si Gun |
| **General characteristics** | | |
| Fuel options | $H_2$, $CH_4$, $C_2H_4$, $C_3H_6$, $C_3H_8$ | Jet-A or Kerosene |
| Combustion pressure | ~ 0.55 MPa (80 PSI) | 0.55 – 0.83 MPa (80 – 120 PSI) |
| Gas velocity | 1800 – 2100 m/s (5900 – 6900 ft/s) | 2000 – 2200 m/s (6500 – 7200 ft/s) |
| Particle velocity | 450 – 600 m/s (1475 – 1975 ft/s) | 475 – 700 m/s (1550 – 2300 ft/s) |
| Powder injection | Axial feed (hotter zone) | Radial feed (cooler zone) |
| Powder injection pressure | Higher | Lower |
| Spray rate | up to 120 g/min (16 lb/h) | up to 200 g/min (26.5 lb/h) |
| **Consumption comparison (typical utility consumption per hour of operation)** | | |
| Fuel | 43800 liters (1670 ft$^3$) $H_2$, or 5280 liters (200 ft$^3$) $C_3H_6$, or 5280 liters (200 ft$^3$) $C_3H_8$ | 28 liters (7.3 gal) kerosene |
| Oxygen | 18420 liters (700 ft$^3$) | 61400 liters (2335 ft$^3$) |
| Water | 600 liters (160 gal) | 2375 liters (625 gal) |

High Velocity Oxy-Fuel (HVOF) Solutions, Oerlikon Metco:
http://www.oerlikon.com/ecomaXL/files/metco/oerlikon_HVOFSolutions_EN6.pdf&download=1
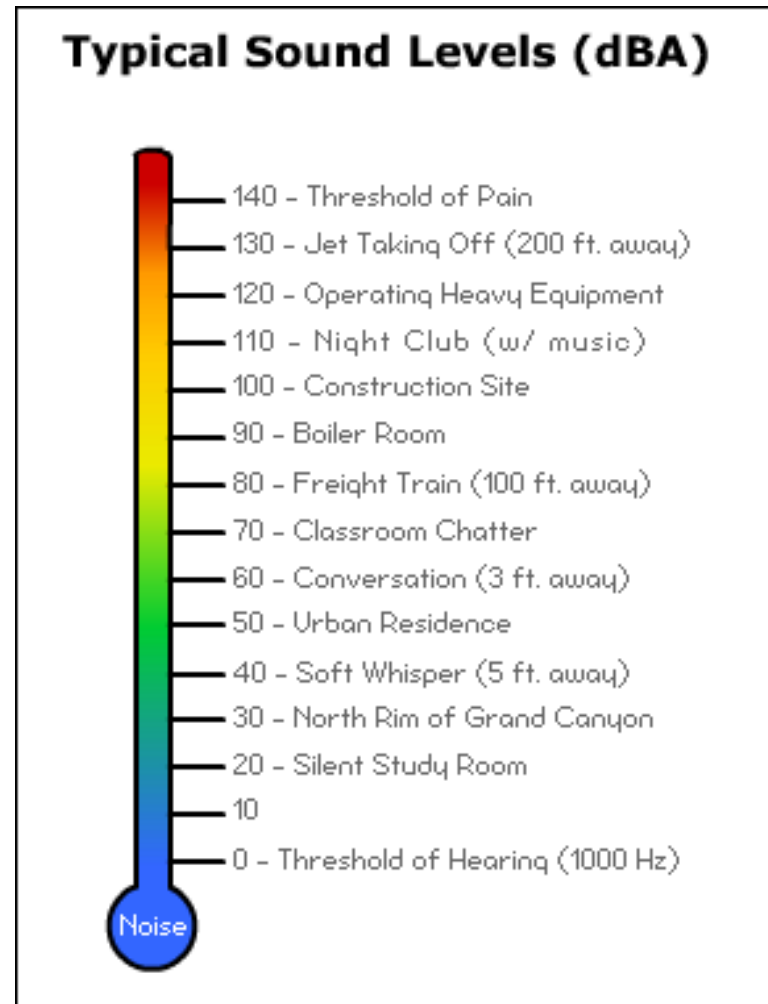
# HVOF Guns



Images courtesy of NRC Canada

Progressive Surface: https://www.youtube.com/watch?v=BS10TaQK0ss&t=4s

# HVOF: Noise (dB)

- Can reach 125 dB

**Typical Sound Levels (dBA)**

- 140 – Threshold of Pain
- 130 – Jet Taking Off (200 ft. away)
- 120 – Operating Heavy Equipment
- 110 – Night Club (w/ music)
- 100 – Construction Site
- 90 – Boiler Room
- 80 – Freight Train (100 ft. away)
- 70 – Classroom Chatter
- 60 – Conversation (3 ft. away)
- 50 – Urban Residence
- 40 – Soft Whisper (5 ft. away)
- 30 – North Rim of Grand Canyon
- 20 – Silent Study Room
- 10
- 0 – Threshold of Hearing (1000 Hz)

Noise
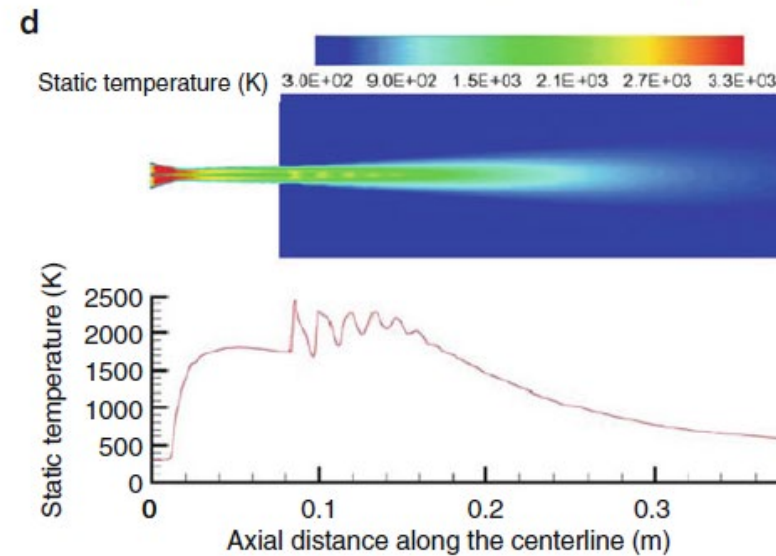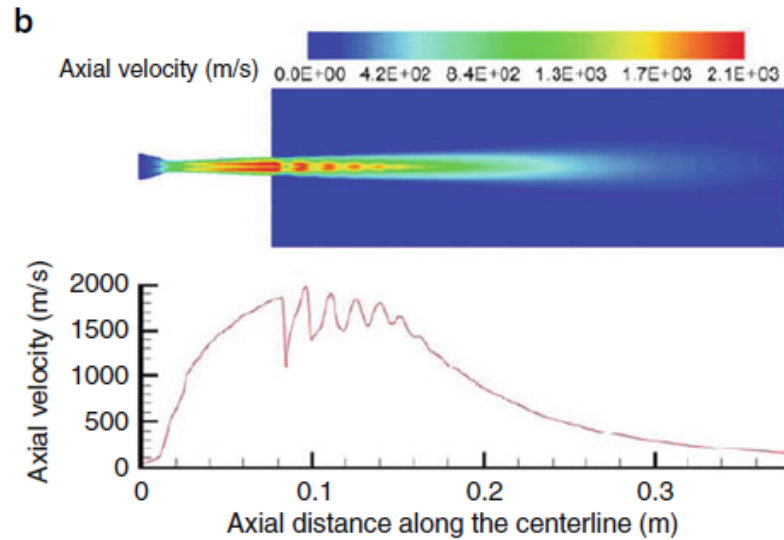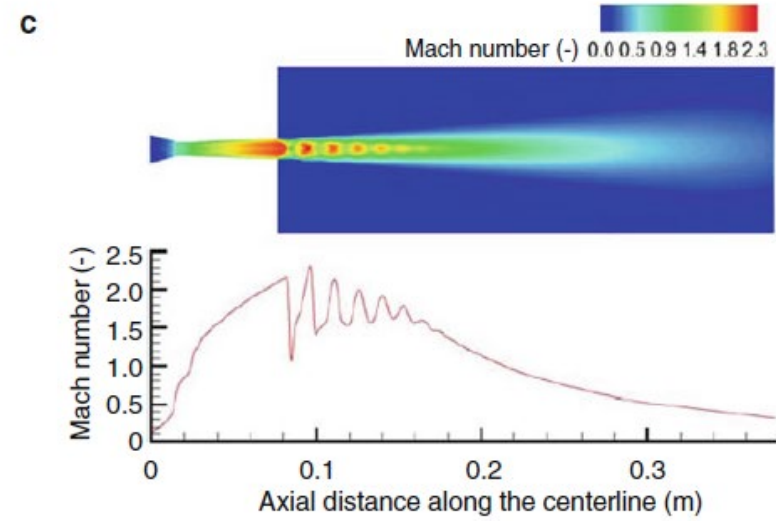
Occupational Safety & Health Administration
https://www.osha.gov/dts/osta/otm/new_noise/#decibles

# Modeled Gas Characteristics
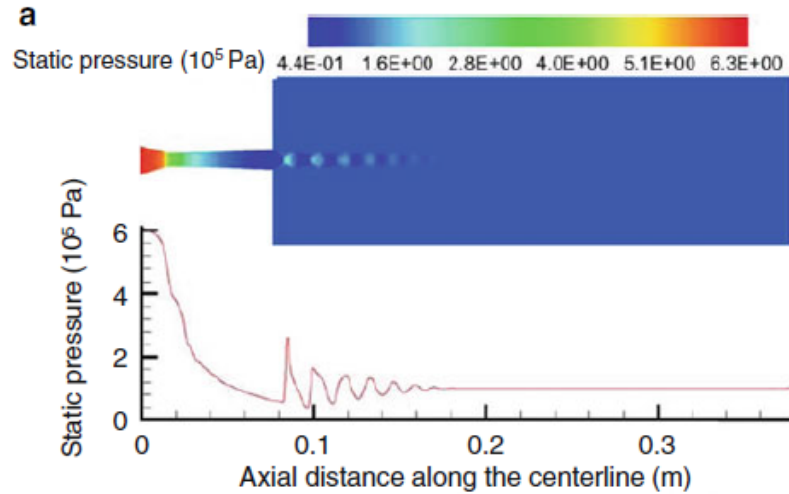
# High Velocity Oxy-Fuel (HVOF)

- Particle characteristics
  - temperature ~ 1500-3000°C
  - speed ~ 300-900 m/s
- Materials - metals and cermets
  - deposition efficiency ~ 45-80%
  - spray rate ~ 1 to 5 kg/hour
- Coating characteristics
  - high density (< 2% porosity)
  - tensile or compressive stress (thick coatings possible)

# Residual Stress

- In thermal spray coatings, residual stress results from:
  - Rapid quenching and concomitant shrinkage of the solidified splat during cooling to the deposition temperature (quenching stress; always in tension
  - Differential thermal contraction stress: when coating and substrate cool together from the deposition temperature to room temperature
  - Volume change due to phase transformation
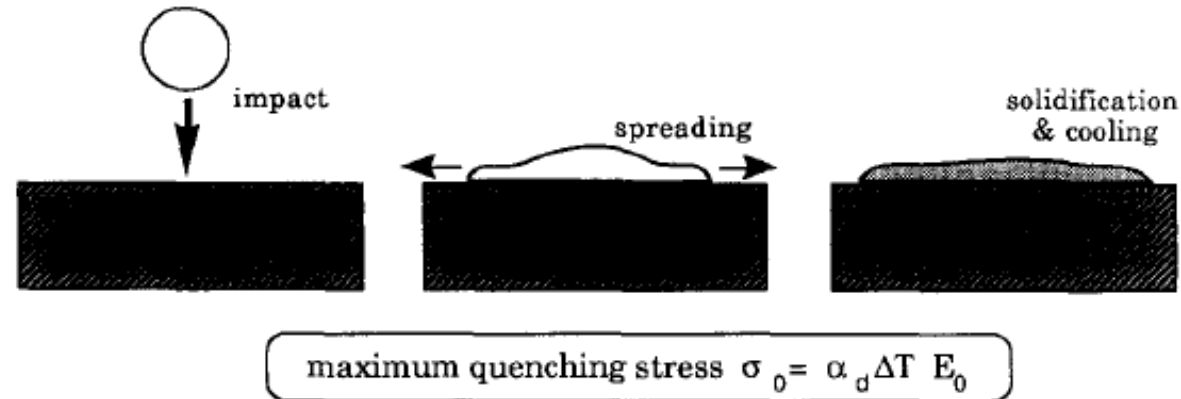  - Peening effect

# Quenching Stress



impact spreading solidification & cooling

maximum quenching stress $\sigma_0 = \alpha_d \Delta T\ E_0$

Fig. 1. Schematic depiction of impact, spreading and cooling of a single splat.

## TABLE I

COMPARISON OF STRAIN AND STRESS FROM THERMAL CONTRACTION FOR A RANGE OF MATERIALS

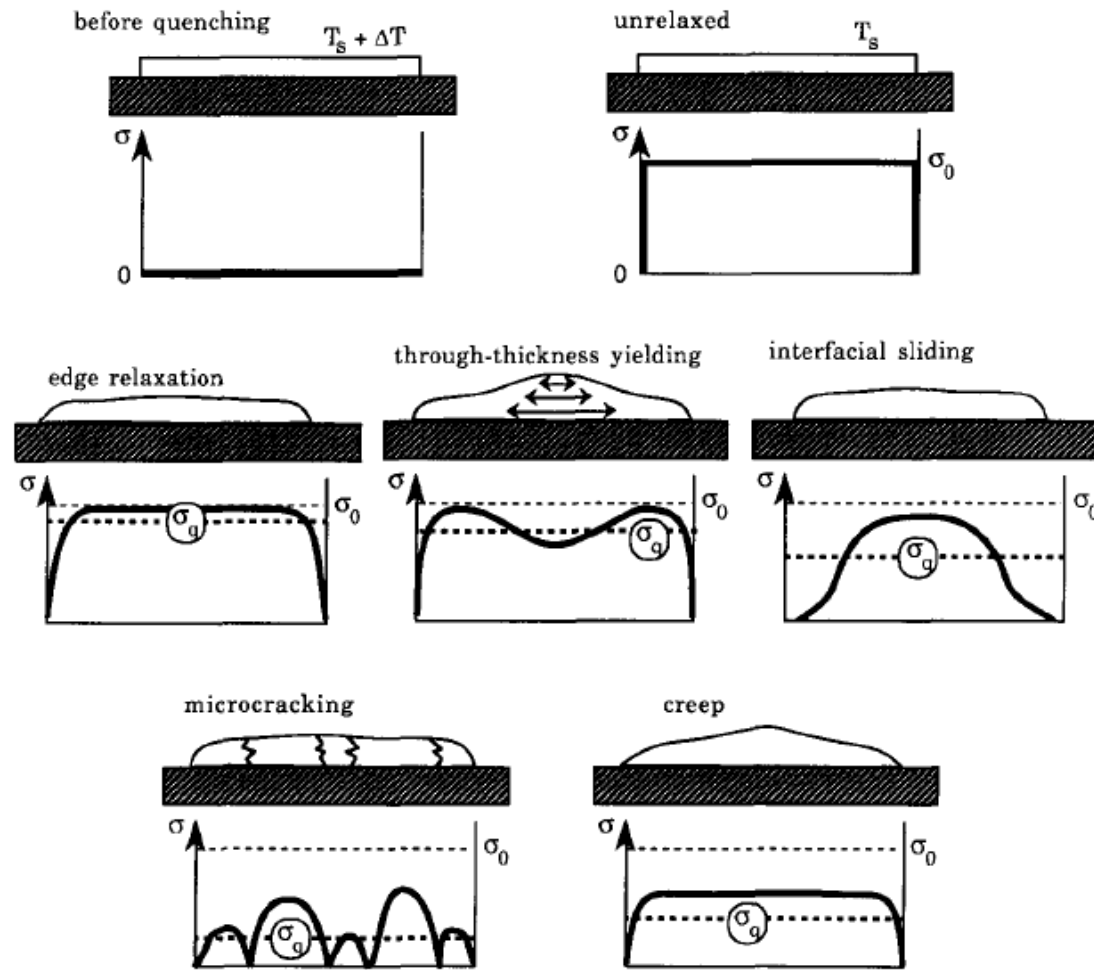| Material | $\alpha_0$ ($10^{-6}\ K^{-1}$) | $E_0$ (GPa) | $\alpha_0 \Delta T$ (mstrain for $\Delta T = 100\ K$) | $\alpha_0 \Delta T E_0$ (MPa) |
|---|---|---|---|---|
| Molybdenum | 4.9 | 325 | 0.49 | 160 |
| Nickel | 12.8 | 200 | 1.28 | 255 |
| Aluminium | 23 | 71 | 2.3 | 162 |
| $Al_2O_3$ | 8 | 370 | 0.8 | 300 |

# Quenching Stress: Relaxation



Fig. 2. Schematic illustration of the stress distributions within a single splat before and after various stress relaxation phenomena have taken place.
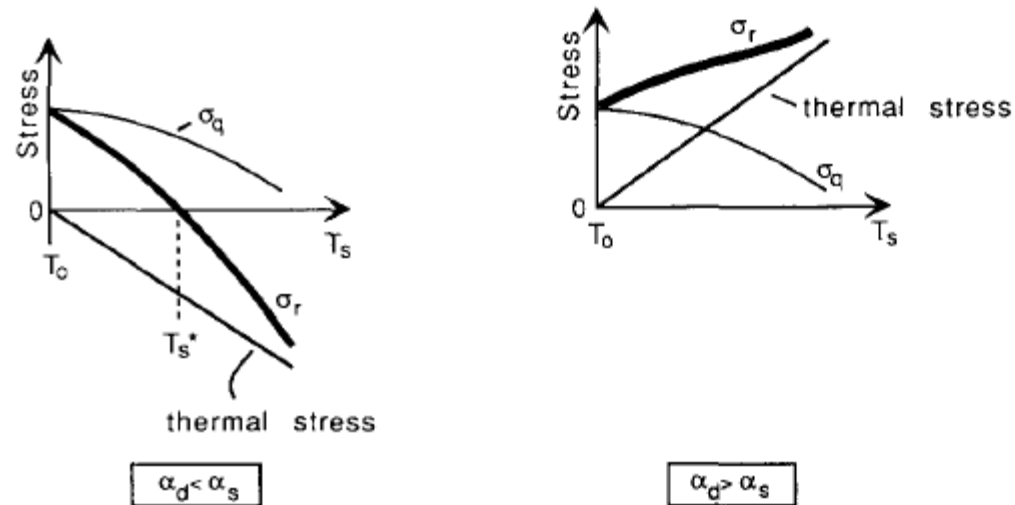
# Residual Stress



Fig. 3. Schematic diagram of the variation of the final residual stress with substrate temperature $T_s$ during spraying. $\sigma_r(T_0)$ is the final residual stress after the sprayed deposit and the substrate cool down to $T_0$.

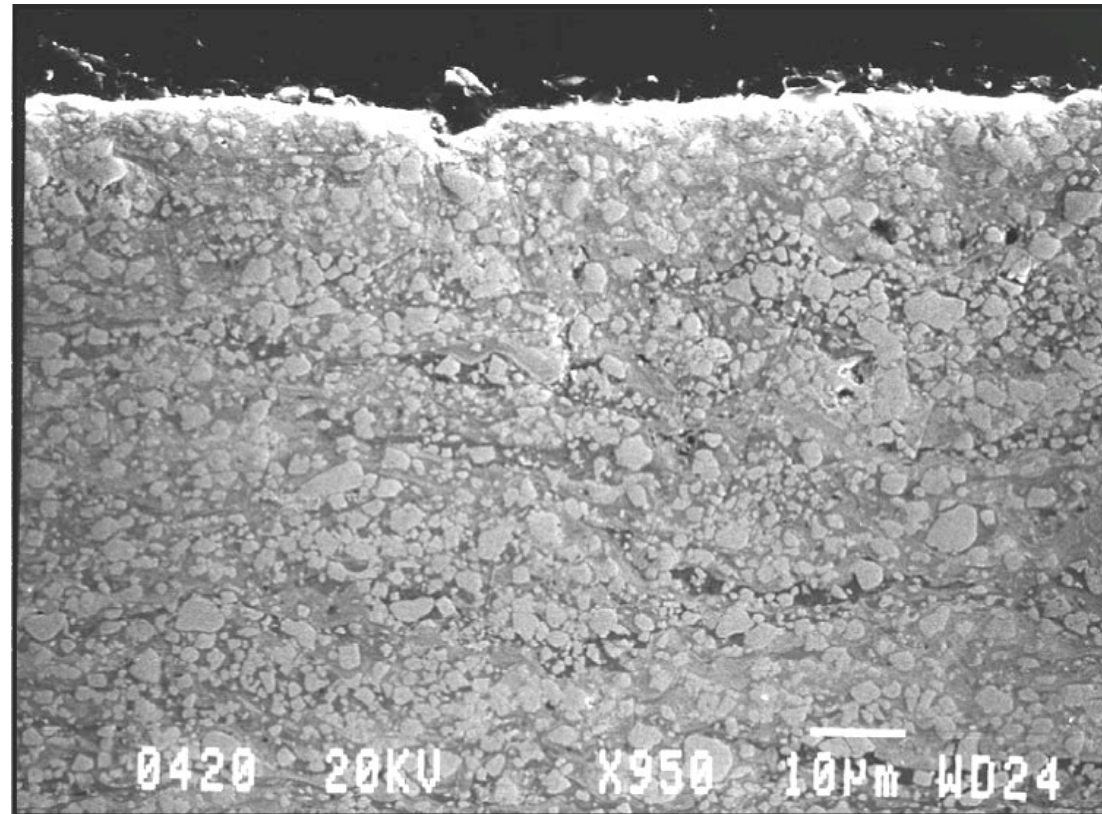$$\sigma_r(T_0) = \{\sigma_q(T_s)/E_d(T_s) + (\alpha_d - \alpha_s)(T_s - T_0)\}E_d(T_0)$$
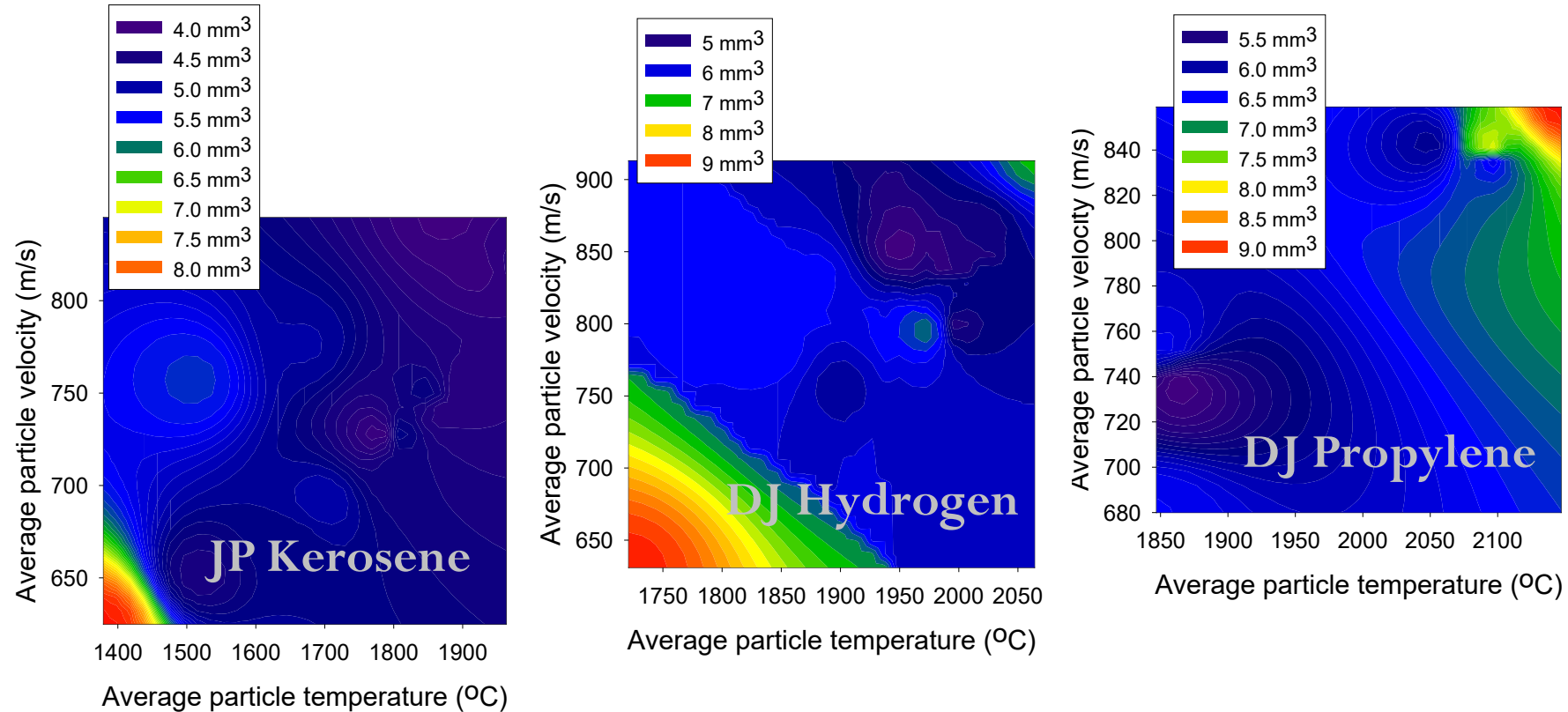
# Residual Stress

- In HVOF, the peening effect is large due to the high impact velocities of the spray particles
- Resulting residual stresses can be in:
  - Compression (liquid fuel)
  - Neutral (gas fuel)
  - Tension (gas fuel)

# HVOF Coating

- Wear-resistant WC-Co coating
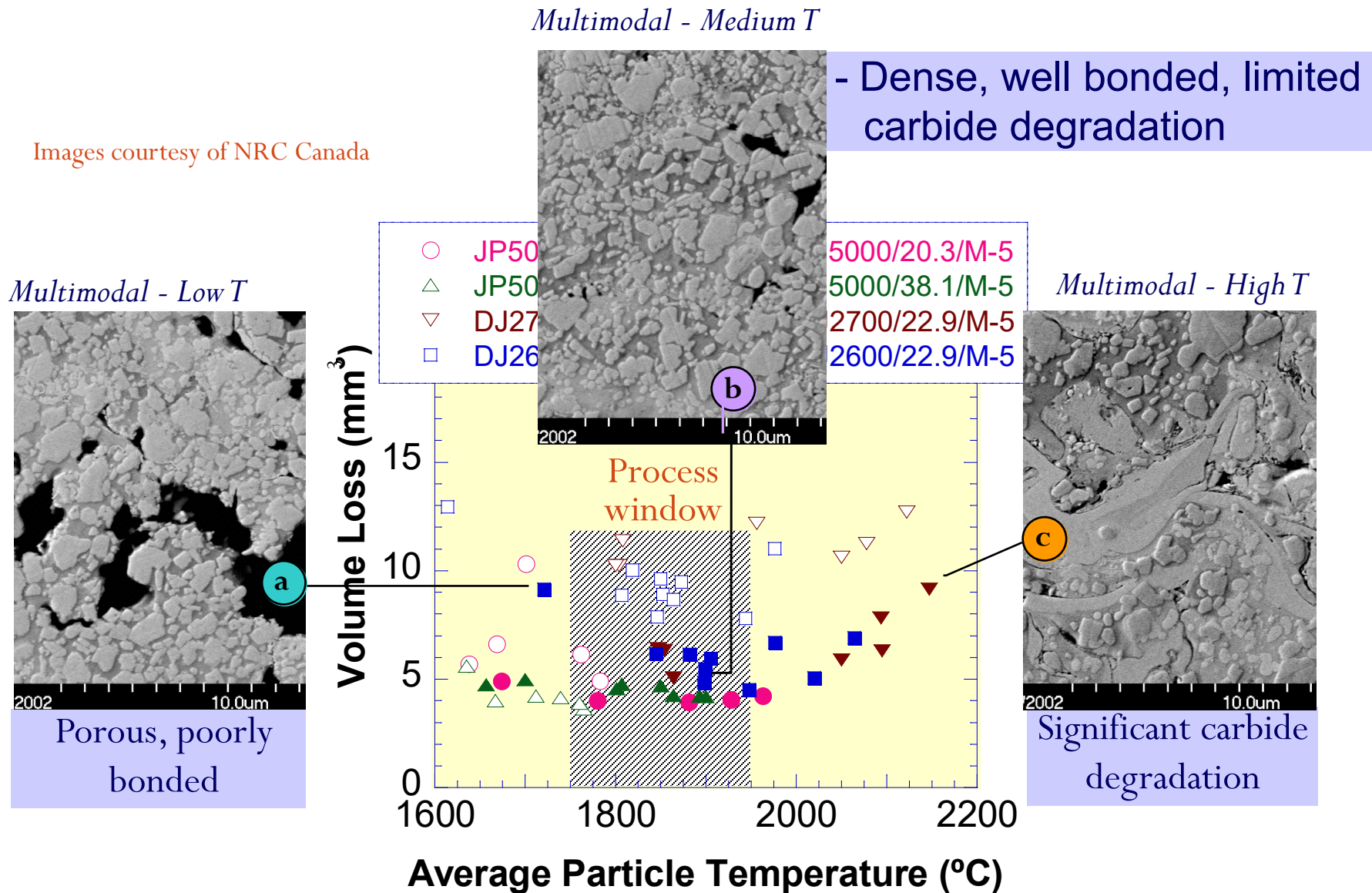
# Abrasion Maps for WC-CO Coatings



- **<u>Optimum region for coating production:</u>**
  - high abrasion resistance
  - robust parameters (small change in performance for large changes in particle conditions

Images courtesy of NRC Canada

66

# Process / Wear Map WC-Co
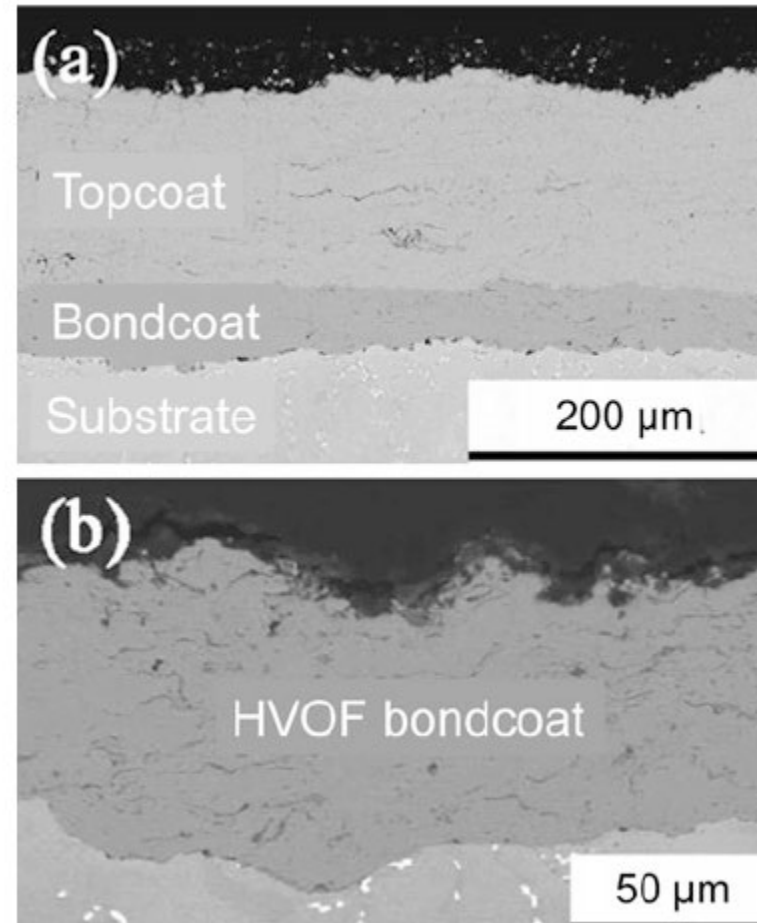
# HVOF Coatings

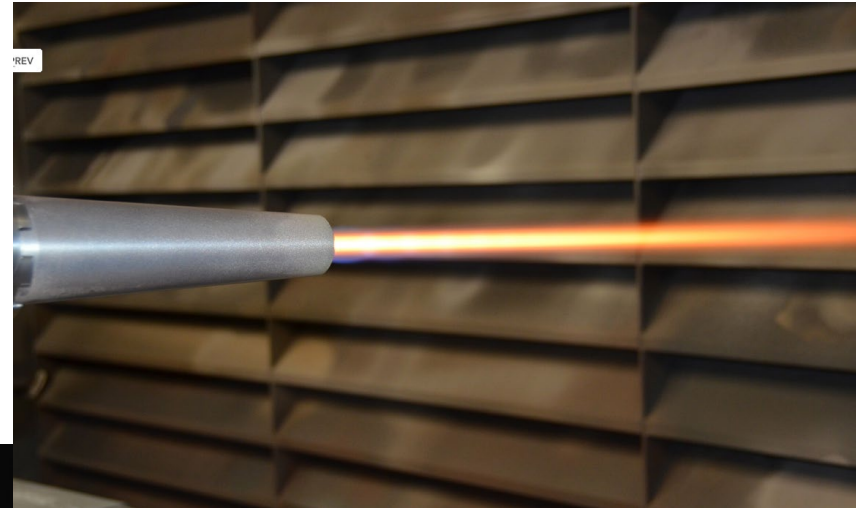- Metals

Fig. 5.38 (a) Cross section of detonation-sprayed TBC using hollow sphere YSZ powder D-gun sprayed with the HVOF bond coat. (b) Microstructure of the HVOF NiCrAlY coating in the as-sprayed state. Reprinted with kind permission from Elsevier [113]

# High Velocity Air-Fuel (HVAF)

- Air is used instead of oxygen
- Many versions developed by Browning

http://uniquecoat.com/

# Arc Spray

# Arc Spray



D.C. power source



Courtesy of Praxair - Tafa

Dual wire rolls

Feeding mechanism and air control

Spray gun

Air
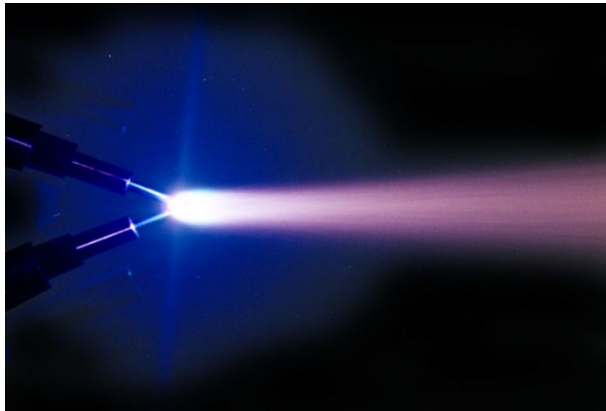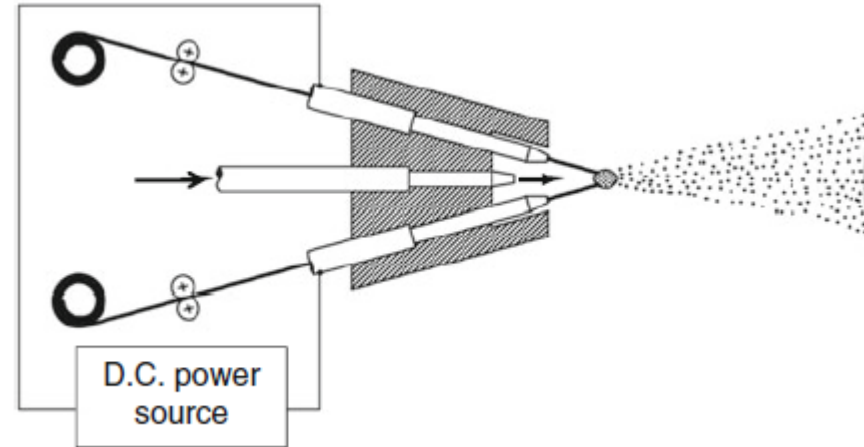
Wires

Compressed Air

D.C. power supply
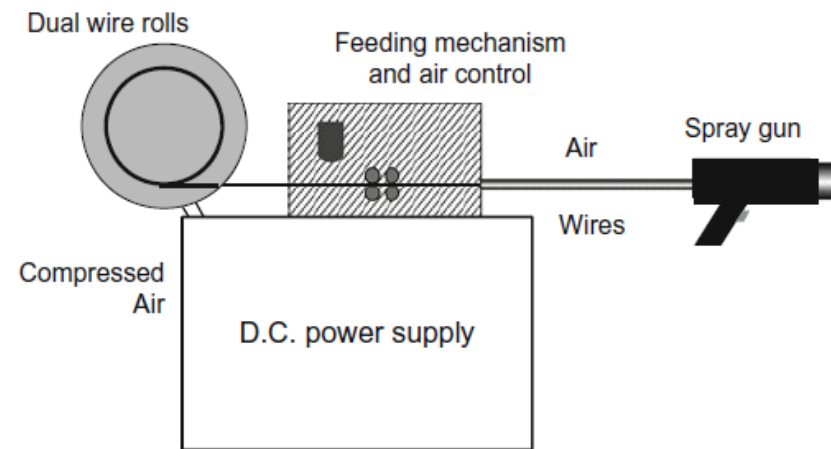
**Fig. 9.3** Schematic of wire arc spray system with power supply, control unit, wire supply rolls, compressed gas line, and torch
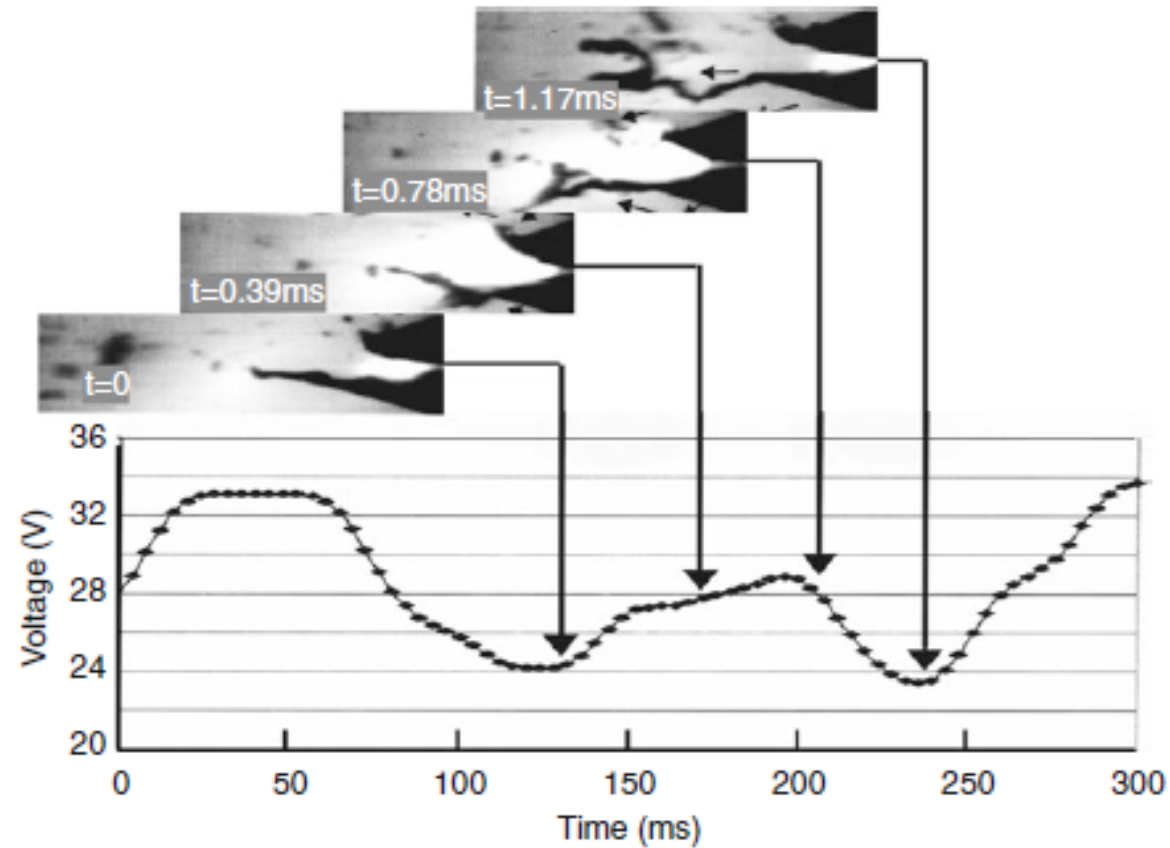
# Atomization Process



**Fig. 9.8** High-speed images of metal droplet formation synchronized with arc voltage trace, showing the forward movement of the anode arc attachment with the associated increase in voltage. Operating parameters: $V = 33$ V, $I = 300$ A, $p = 69$ kPa [40] (Copyright © ASM International. Reprinted with permission)

# Primary and Secondary Gas Flows



Fig. 9.6 Schematic of wire arc spray head with primary and secondary gas flow (Reproduced with kind permission of Praxair TAFA)

secondary gas

Primary gas
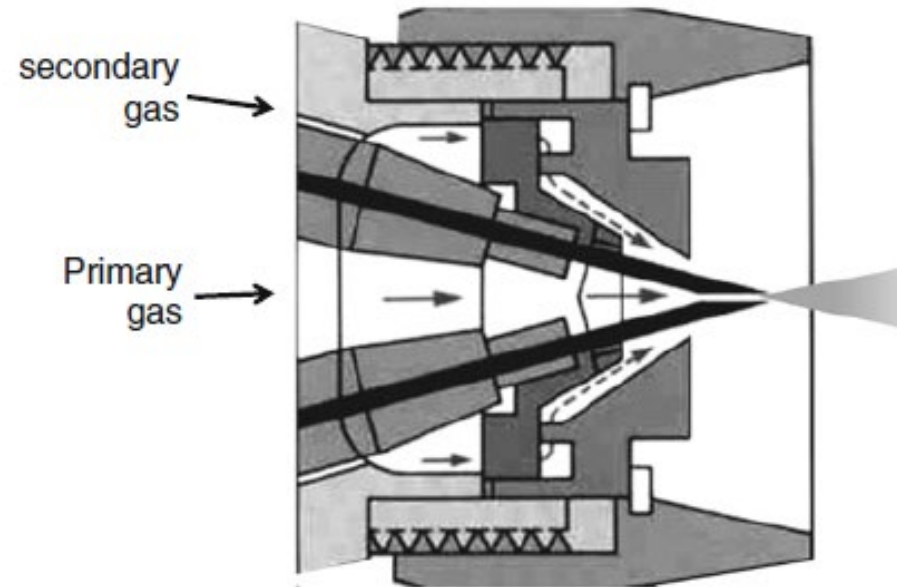
**Typical Spray Conditions**

- Arc voltage:             20–40 V
- Arc current:             100–400 A
- Wire feed speed:         7–10 m/min
- Standoff distance:       10–20 cm
- Gases:                   Air, nitrogen, CO2
- Gas flow rates:          800–2,400 slm
- Gas supply pressure:     0.27–0.6 MPa

# Arc Spray
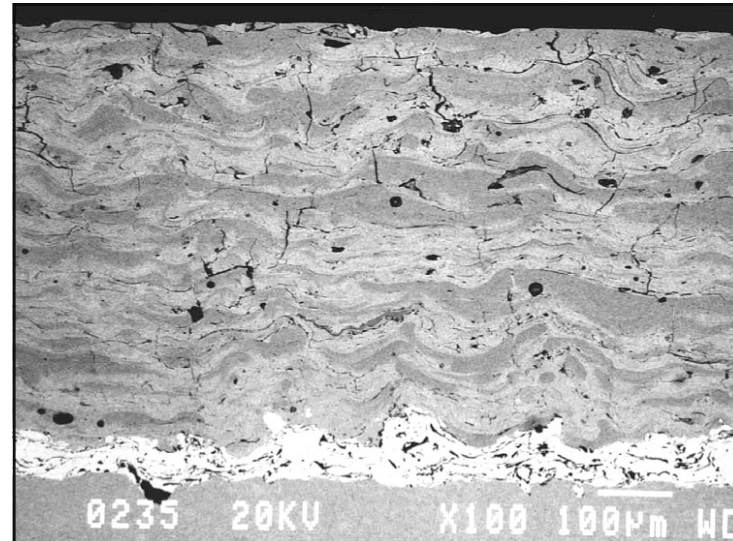
# Arc Spraying

- Particle characteristics
  - temperature ~ 1500-3000°C
  - speed ~ 50-200 m/s
- Materials - metals and cermets
  - spray rate ~ 5 to 50 kg/hour
- Coating characteristics
  - density ~ 5 to 20% porosity
  - Relatively high oxide content
  - Low cost

# Wire for Arc Spray

- Metals, alloys and cored wires
- Examples from Praxair:

  https://www.praxairsurfacetechnologies.com/en/materials-and-equipment/materials/wires

**Pure metal and metal alloy wires**

- » Nickel-based wires
- » Iron-based wires
- » Aluminum-based wires
- » Copper-based wires
- » Zinc-based wires
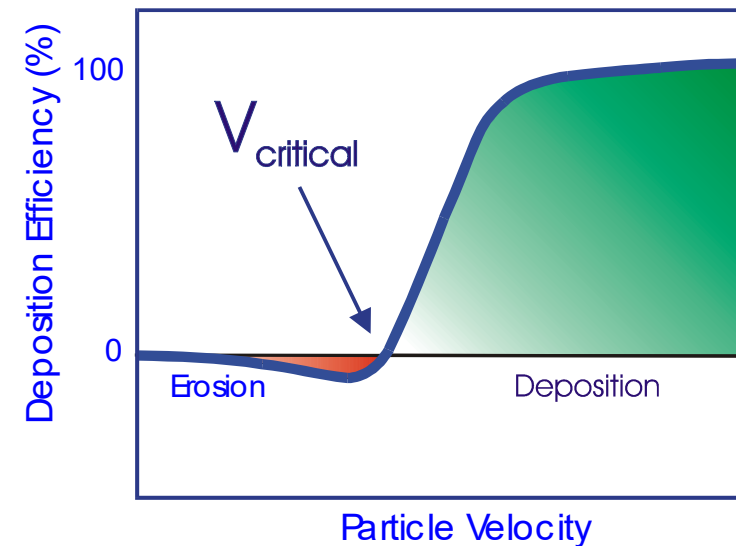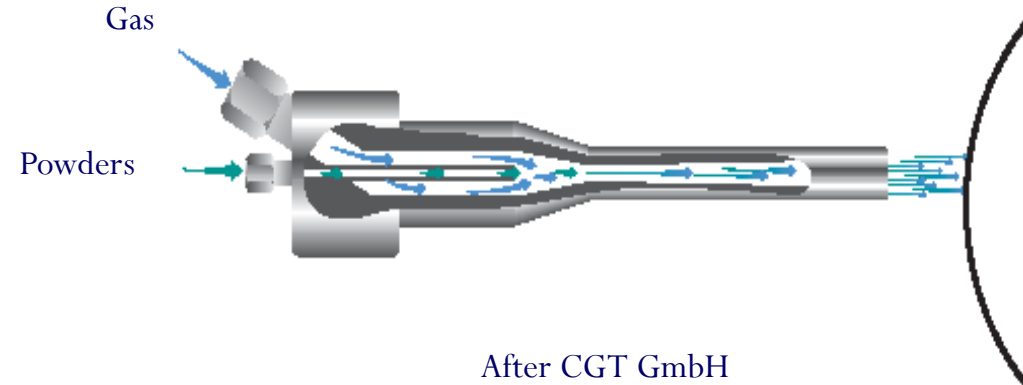- » Specialty wires, such as titanium, molybdenum, and indium

**Cored wires**

- » Nickel-based cored wires
- » Iron-based cored wires
- » Cobalt-based cored wires
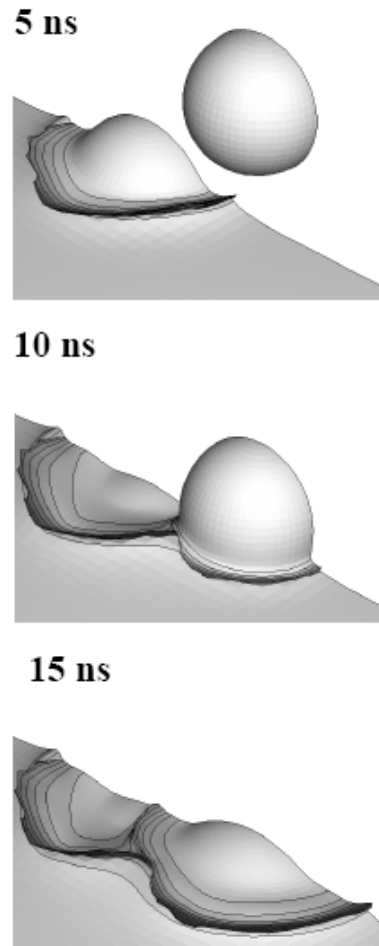- » Tungsten-cored wires
- » Nano-composite cored wires

# Cold Spray

# Cold Spray: A Solid State Deposition Process

- A high-velocity low-temperature gas jet accelerates particles

- The impact velocity is high enough for "cold welding" the particles forming a coating

- Main advantages:
  - Very low oxidation
  - No grain growth or phase transformation

Gas

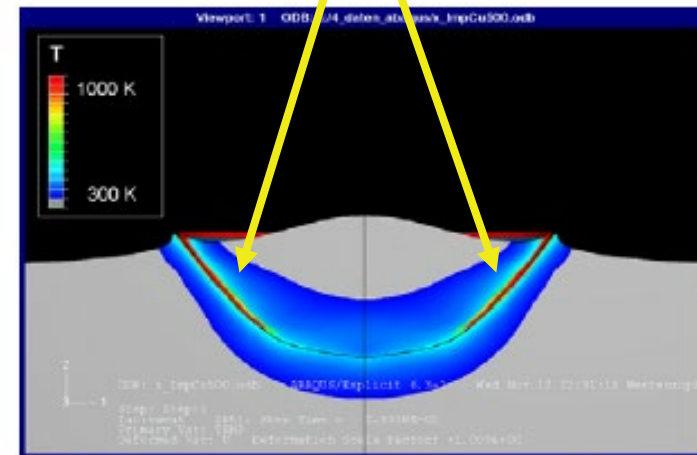Powders

After CGT GmbH

$V_{critical}$

Deposition Efficiency (%)

100

0

Erosion

Deposition

Particle Velocity

# Impact Deformation and Welding



5 ns

10 ns

15 ns

F. Gärtner, *et al.*

**Adiabatic shear instability**

Tobias Schmidt et al

# Operation Parameter

| | |
|---|---|
| Stagnation jet pressure, MPa (psi) | 1–4 (145–600) |
| Stagnation jet temperature, °C (°F) | 0–1000 (32–1832) |
| Gas flow rate, $m^3$/min ($ft^3$/min) | 1–2 (35–70) |
| Powder feed rate, kg/h (lb/h) | 2–8 (4–18) |
| Spray distance, mm (in.) | 10–50 (0.4–2) |
| Power consumption, kW (for heating gas) | 5–25 |
| Particle size, μm | 1–50 |

After ASM Handbook 5A p. 55

# Cold Spray Deposition
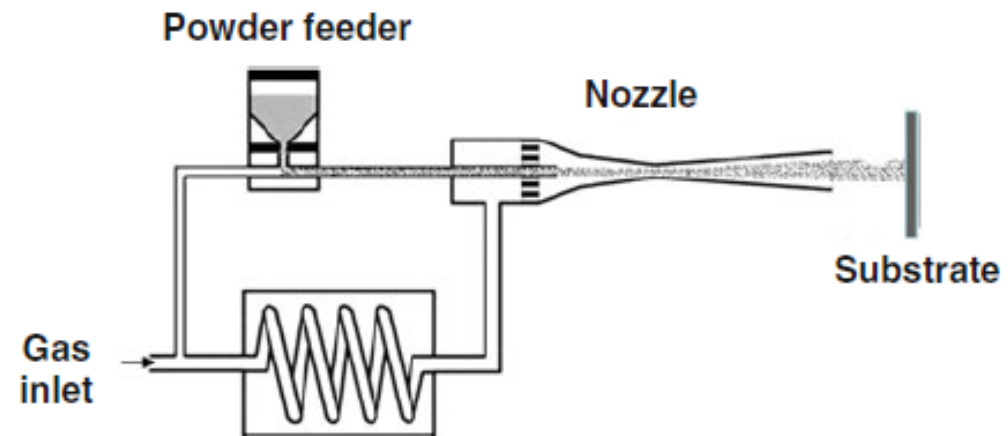


*Courtesy of NRC Canada

# Cold Spray

- Particle characteristics
  - temperature ~ 0-100°C
  - speed ~ 400-1000 m/s
- Materials - metals and cermets
  - spray rate ~ 3 to 5 kg/hour
- Coating characteristics
  - density ~ 1-10 % porosity
  - No oxidation, no phase change

# Low and High Pressure Cold Spray Systems



Low Pressure Cold Spray:
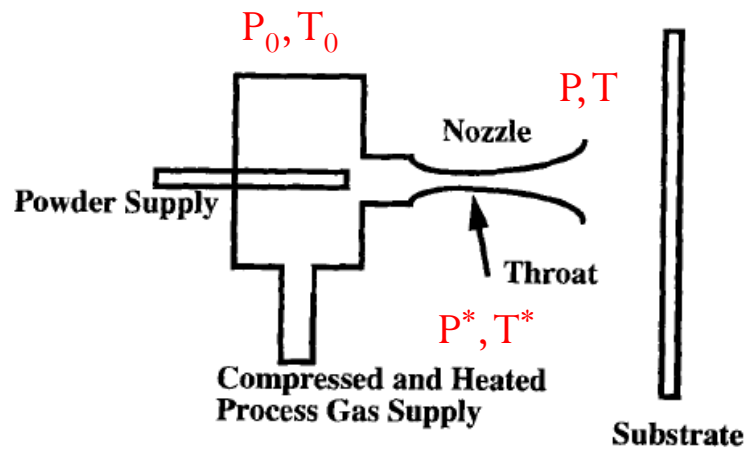After J. Villafuerte,
Centerline Canada
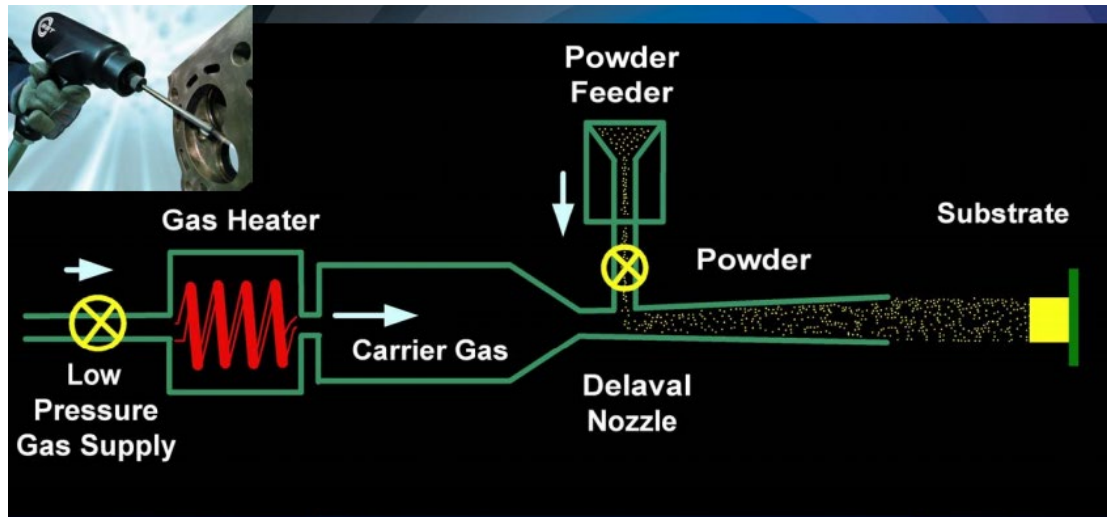
High Pressure Cold Spray

# One-dimensional Isentropic Flow

- Well described in "Gas Dynamic Principles of Cold Spray, R.C. Dykhuizen and M.F. Smith, JTST 7(1998)205-2012

- $\dot{m}$ = mass flow rate fixed
- ▢ = ratio of specific heats (1.66 or 1.4 for monoatomic or diatomic gases)
- $M$ = Mach number
- R = Universal gas constant/gas molecular weight

$P_0, T_0$

$P, T$

Nozzle

Powder Supply

Throat

$P^*, T^*$

Compressed and Heated
Process Gas Supply

Substrate

0 = stagnation
* = Throat

# One-dimensional Isentropic Flow

- At the throat $M = 1$ (choked flow)

$$\frac{T_o}{T*} = 1 + \frac{\gamma - 1}{2} \qquad V* = \sqrt{\gamma R T*} \qquad \rho* = \frac{\dot{m}}{V* A*}$$

$$P* = \rho* R T* \qquad \frac{P_o}{P*} = \left(1 + \frac{\gamma - 1}{2}\right)^{\gamma/(\gamma - 1)}$$

- At the nozzle exit (assuming P < atm, overexpanded flow)

$$\frac{A}{A*} = \left(\frac{1}{M}\right)\left[\left(\frac{2}{\gamma + 1}\right)\left(1 + \frac{\gamma - 1}{2} M^2\right)\right]^{(\gamma+1)/[2(\gamma-1)]} \qquad \frac{P}{P*} = \left(\frac{\gamma + 1}{2 + (\gamma - 1) M^2}\right)^{\frac{\gamma}{(\gamma-1)}}$$

$$\frac{T_o}{T} = 1 + \frac{\gamma - 1}{2} M^2 \qquad V = M\sqrt{\gamma R T} \qquad \frac{\rho_o}{\rho} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{1/(\gamma-1)}$$

# Particle Acceleration

- Particle acceleration due to drag force:

$$m\frac{dV_p}{dt} = mV_p\frac{dV_p}{dx} = \frac{C_D A_p \rho(V-V_p)^2}{2}$$

- For low values of the spray particle velocity (as compared to the gas velocity):

$$V_p = V\sqrt{\frac{C_D A_p \rho x}{m}}$$

# Cold Spray Modeling



Fig. 6.13 Gas temperature, $T_g$, and velocity, $v_g$, evolutions along the nozzle axis for a $N_2$ flow ($T_0 = 573$ K, $p_0 = 2.5$ MPa, standard nozzle), and Cu particle (15 μm) velocity, $v_p$ and temperature, $T_p$, evolutions along the axis (* nozzle throat, E nozzle exit, S substrate). Reprinted with kind permission of ASM [31]
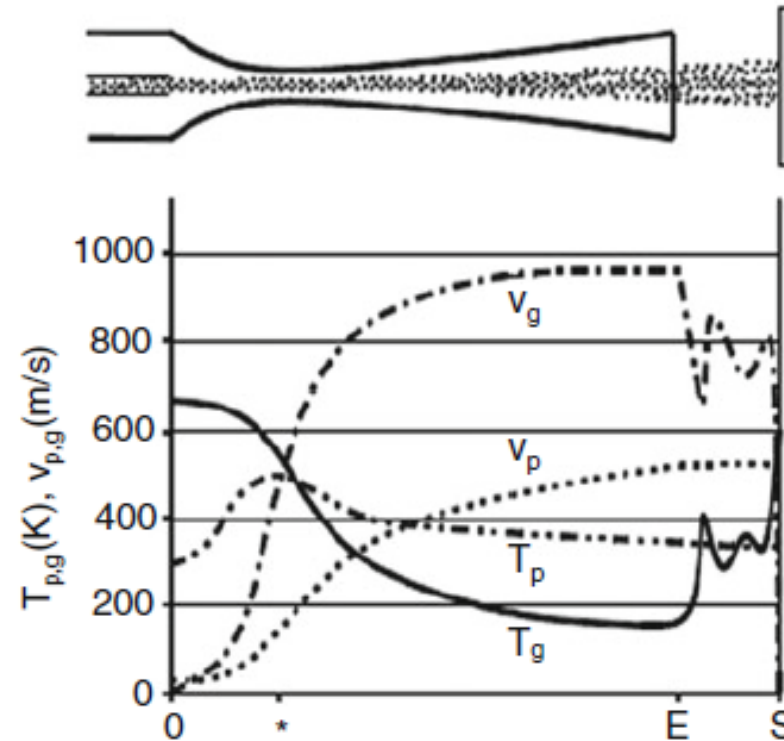
# Cold Spray Modeling



Fig. 6.15 Dependence of the particle temperature and velocity at the nozzle exit with the inlet gas pressure for a standard nozzle, an initial temperature of 673 K and $N_2$ gas. Reprinted with kind permission of ASM [31]
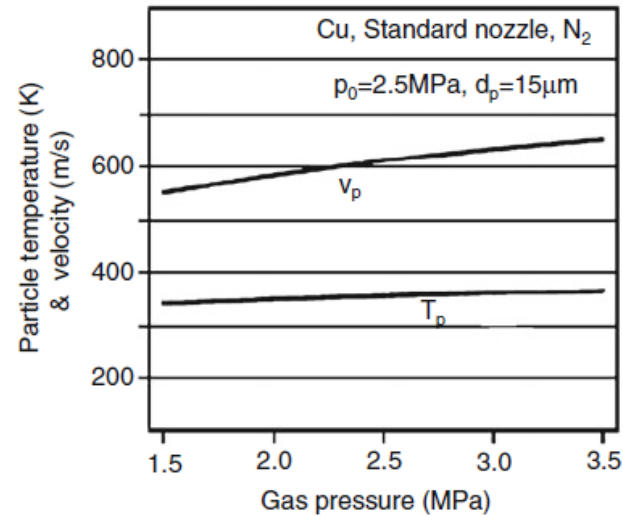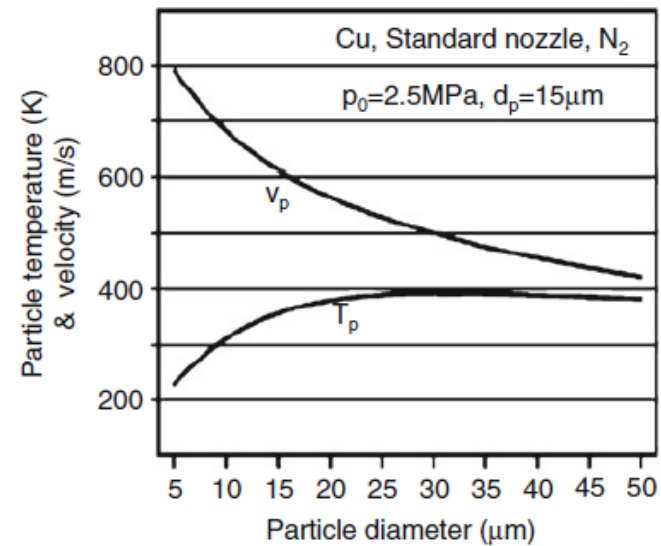


Fig. 6.16 Dependence of the Cu particle temperature and velocity on its size at the nozzle exit: standard nozzle, $N_2$ as process gas, 2.5 MPa, 673 K. Reprinted with kind permission of ASM [31]
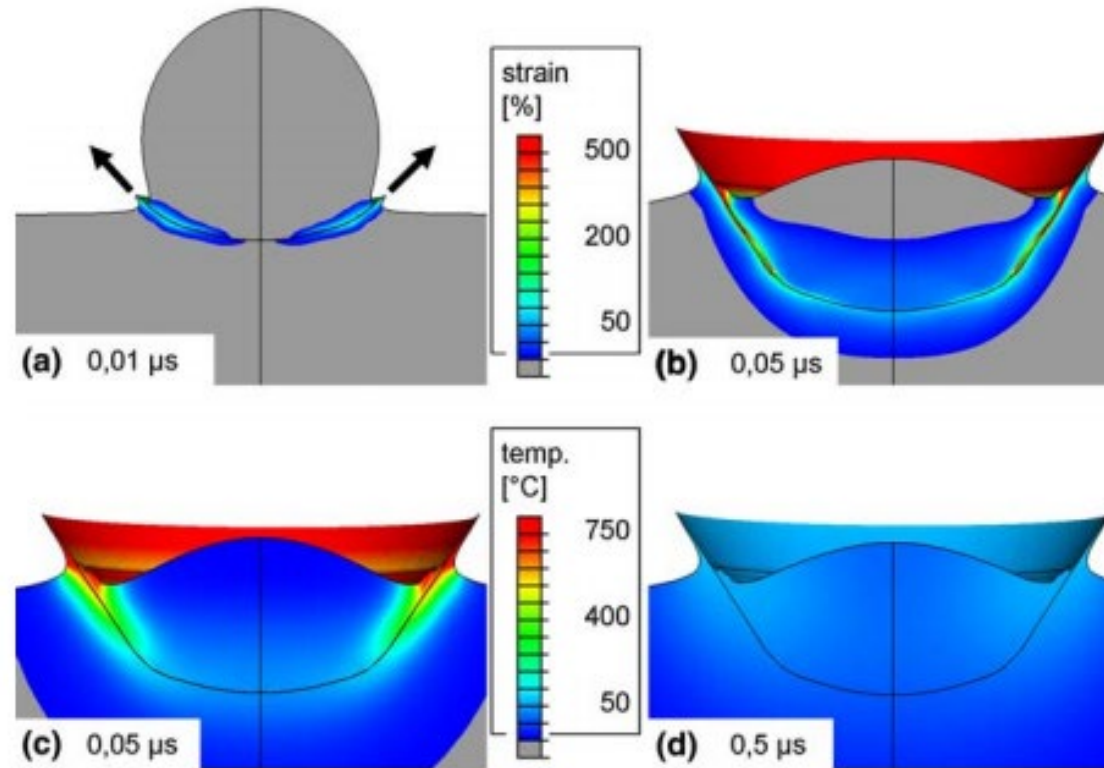
# Shear Instability



**Fig. 11** Single sequences of an impact of a 25 μm Cu particle to a Cu substrate with 500 m/s at an initial temperature of 20 °C. (a, b) Strain field and (c, d) temperature field. For the analysis a thermally coupled axisymmetric model was used

T. Schmidt et al., JTST, 18 (2009) 794–808

# Fundamental investigation of impact behavior
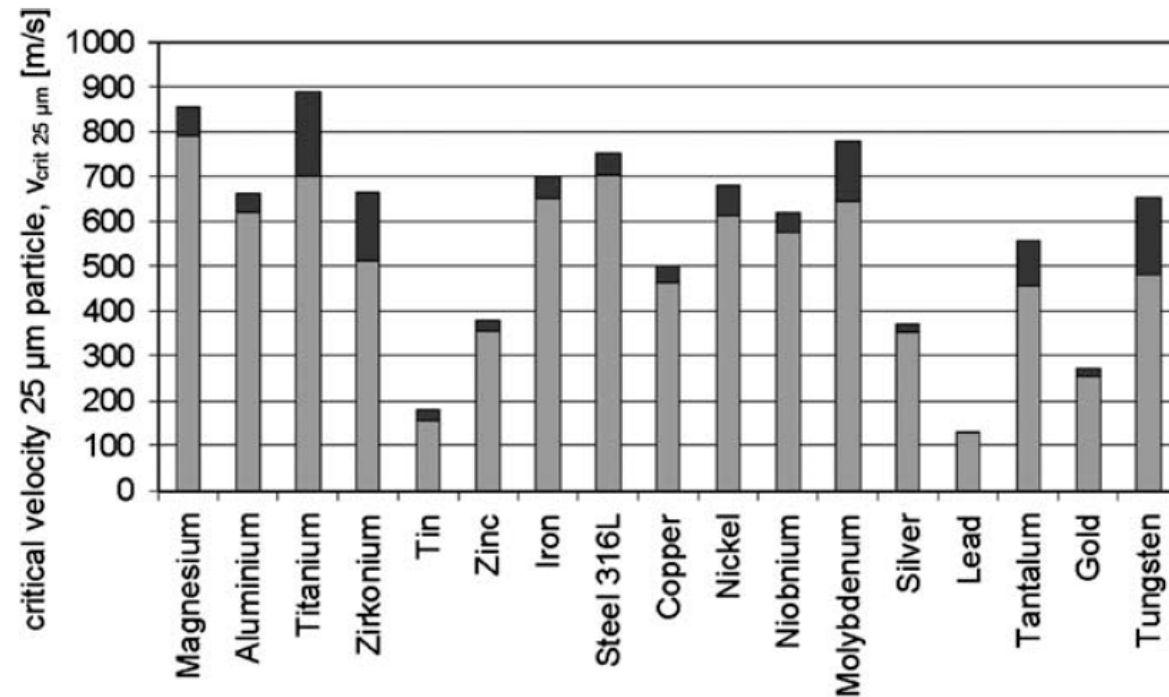
**Critical velocity (d=25 μm)**

$$v_{\text{crit}}^{\text{th,mech}} = \sqrt{\frac{F_1 \cdot 4 \cdot \sigma_{\text{TS}} \cdot \left(1 - \frac{T_i - T_R}{T_m - T_R}\right)}{\rho} + F_2 \cdot c_p \cdot (T_m - T_i)}$$
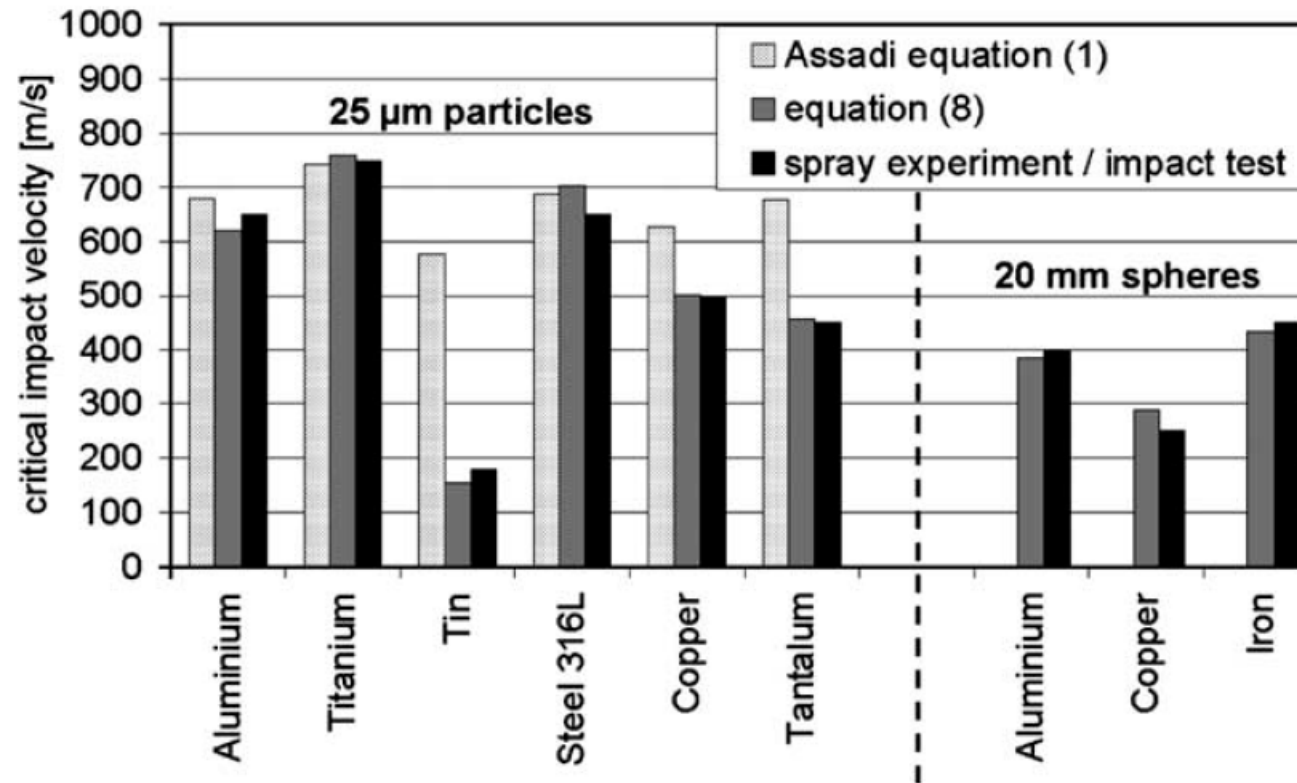
$F_1$, $F_2$: empirical factors
$\sigma_{\text{TS}}$: tensile strength
$T_i, T_R, T_m$ :initial, reference
and melting temperatures
$c_p$: specific heat



T. Schmidt *et al.*, Acta Materialia, **54** 729-742, **(2006)**

$$v_{\text{cr}} = 667 - 14\rho_{\text{part}} + 0.08T_m + 0.1\sigma_u - 0.4T_i$$

**Assadi *et al.*, Acta Materialia, 51**, 4379–4394 **(2003)**

**Critical velocity (experiment vs modeling)**

# Effect of Particle Size



Fig. 6.27 Temporal evolution of the temperature at the monitored volume (sheared interface) of copper particles with different impact velocities and two sizes: (a) 5 μm and (b) 25 μm. Reprinted with kind permission from Springer Science Business Media [45], copyright © ASM International
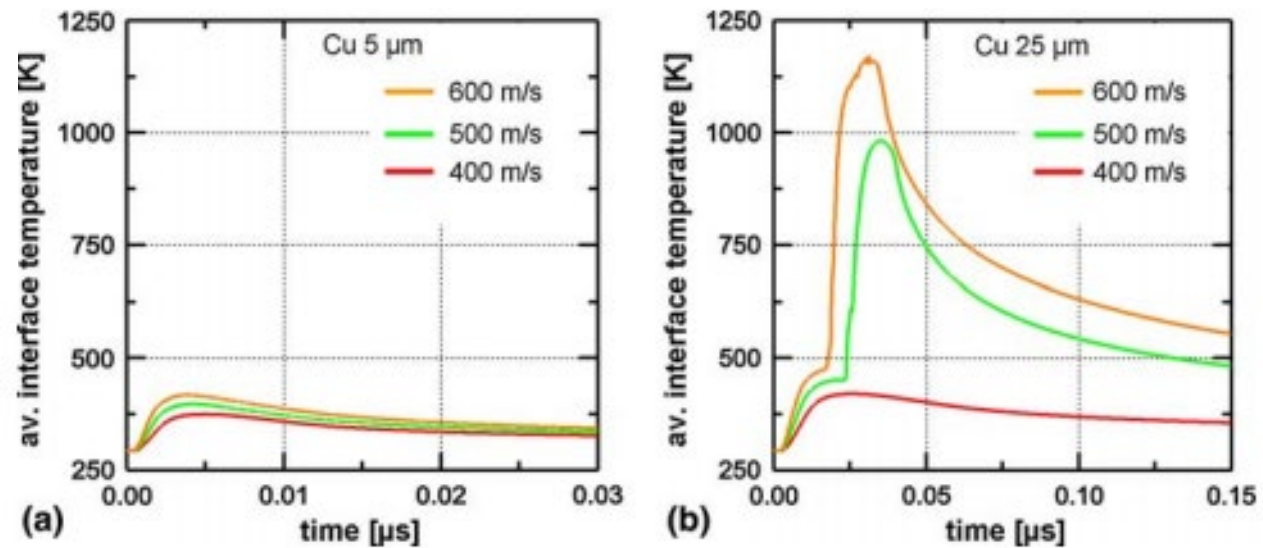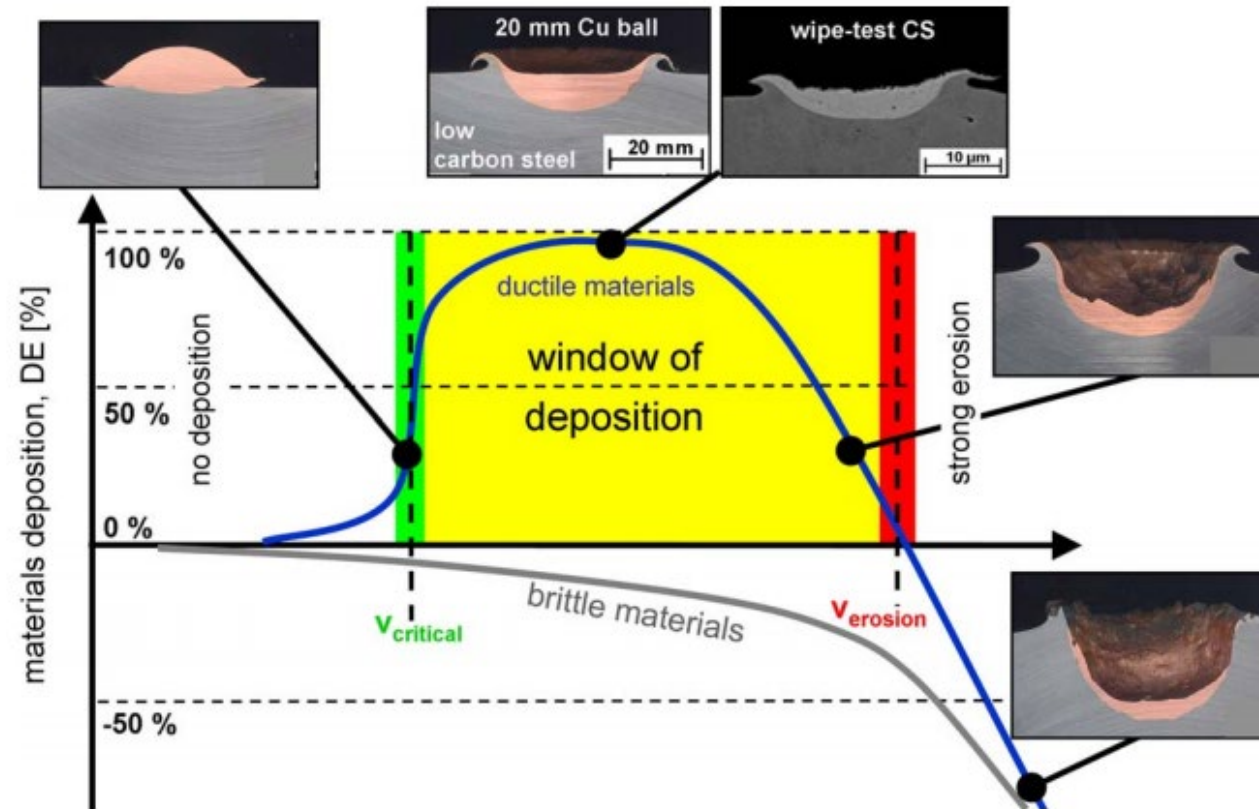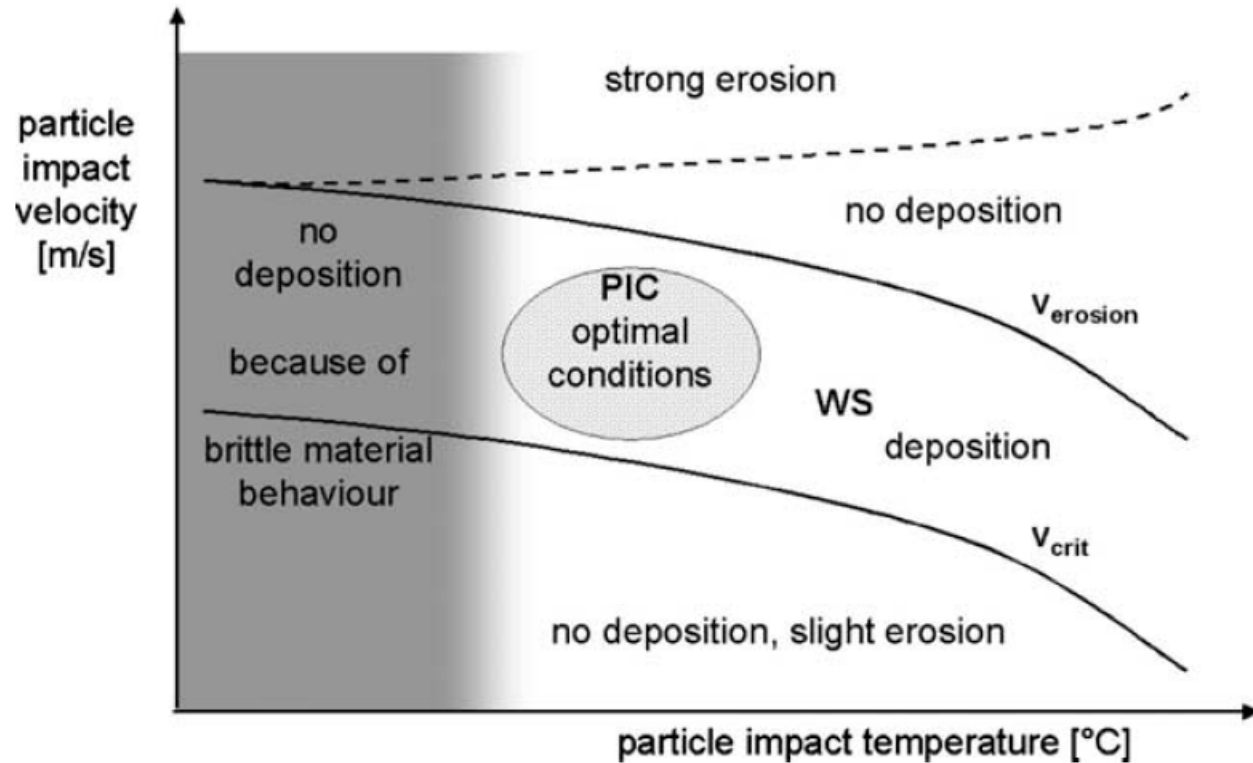
T. Schmidt et al., JTST, 18 (2009) 794–808

**Fig. 8** Schematic correlation between particle velocity, deposition efficiency (DE) and impact effects for a constant impact temperature. Deposition is only observed for ductile materials in a certain velocity range for a given powder size and temperature, the so-called "window of deposition"

T. Schmidt et al., JTST, 18 (2009) 794–808

particle impact velocity [m/s]

strong erosion

no deposition

no deposition because of brittle material behaviour

PIC optimal conditions

$V_{erosion}$

WS deposition

$V_{crit}$

no deposition, slight erosion

particle impact temperature [°C]

WS = Window of sprayability
PIC = Particle impact condition

**Ductile to Brittle Transition**
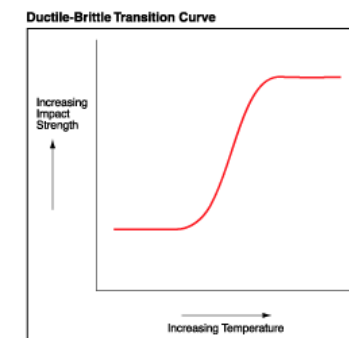
T. Schmidt *et al.*, Acta Materialia, **54** 729-742, **(2006)**
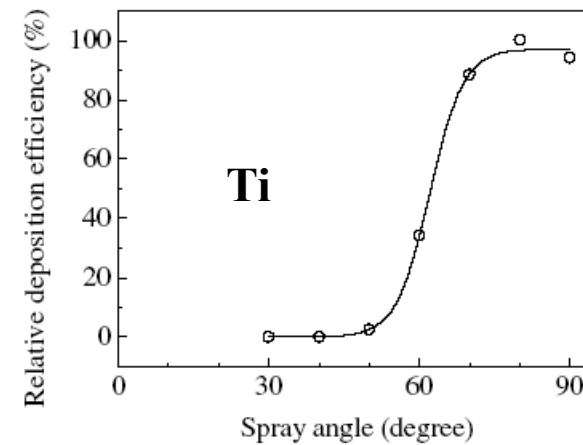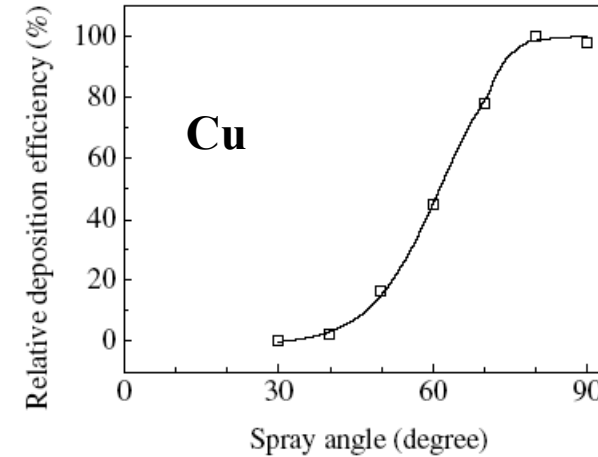
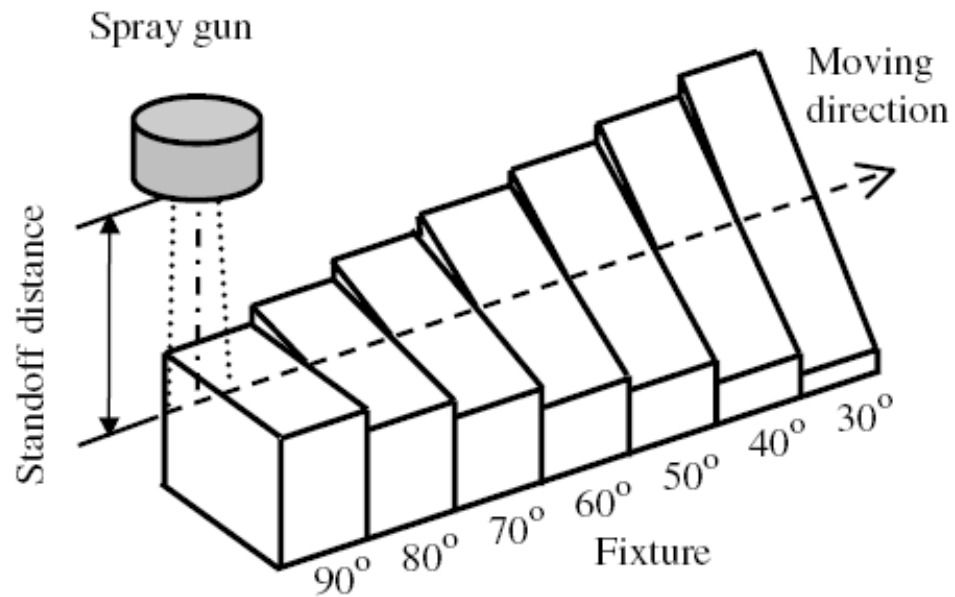**Exemple: Tin**

$T_{trans}$=13°C

**Temperature range
50-200 °C**

**At 50 °C
v ~ 150-340 m/s**

**At 200 °C
v ~ 70-150 m/s**



Ductile-Brittle Transition Curve

Increasing Impact Strength

Increasing Temperature

# Effect of angle of deposition



**C. J. Li *et al.* ITSC 2003: International Thermal Spray Conference, pp.pp. 91-96, (2003)**
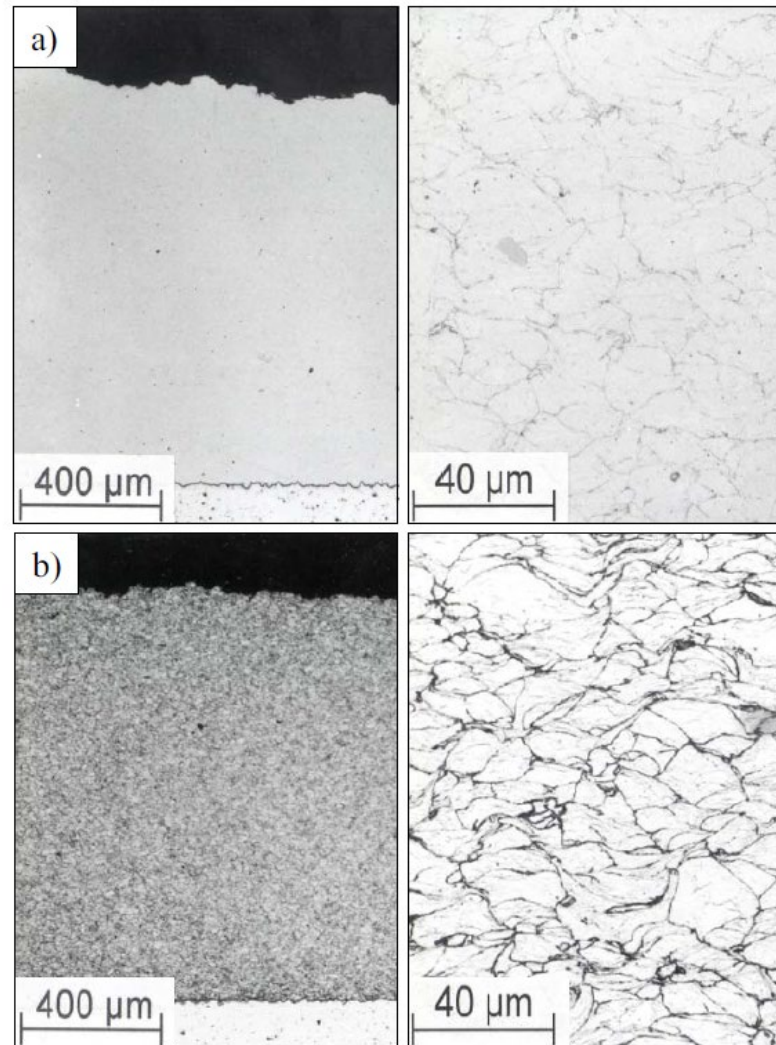
# Coating Structure: Aluminum



Figure 7: Microstructure of a Cu coating Cold Gas sprayed using N₂ as process gas onto an Al substrate, a) as-polished and b) etched.O
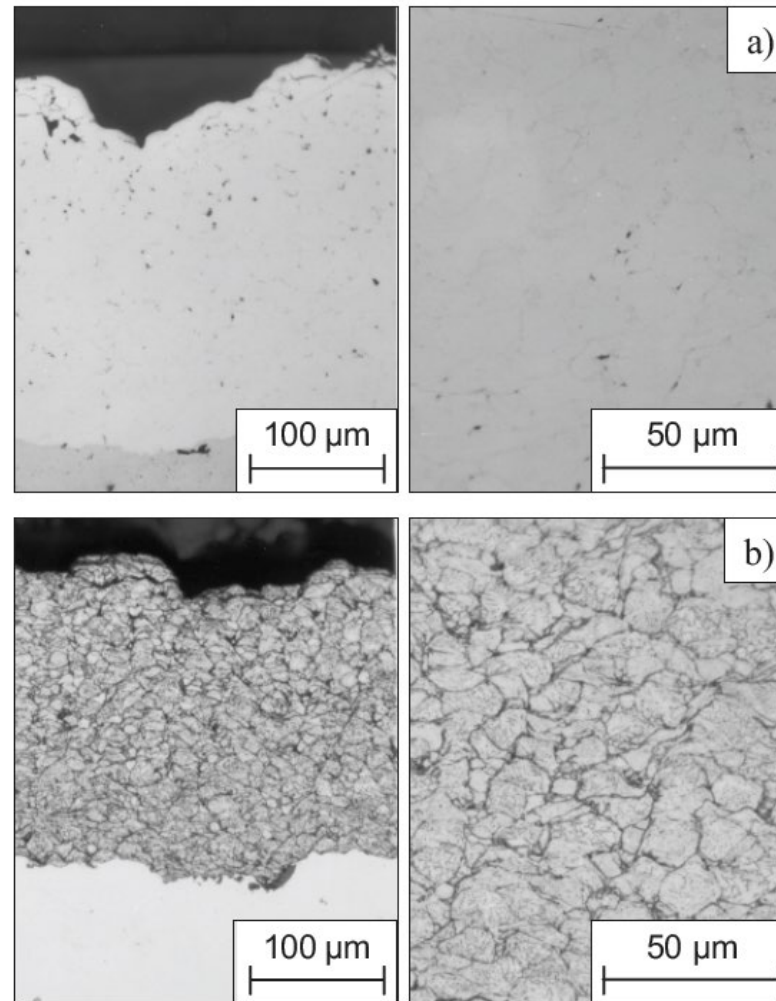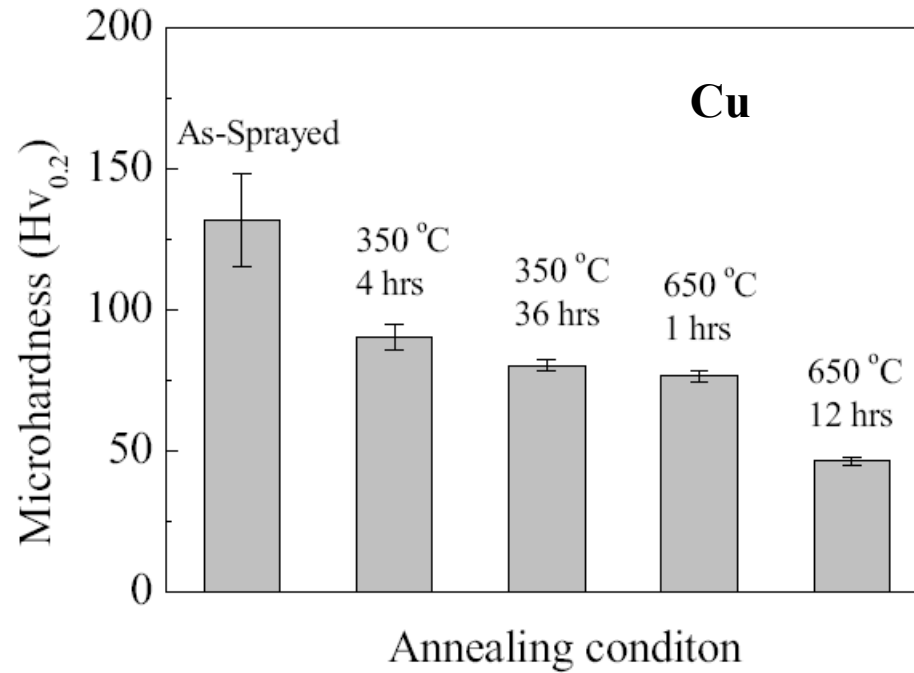
# Coating Structure: 316L Steel



*Figure 9: Microstructure of a 316L coating Cold Gas sprayed using $N_2$ as process gas onto an Al substrate: a) as-polished and b) etched.O*

Steel:
Microhardness
As sprayed : 193 HK
Annealed (1100C 24h): 105-115 HK
Mild steel sheet : 120 HK

Cu:
Microhardness
As sprayed : 153 HK
Annealed (650C 24h): 52 HK

**CS Coatings have higher hardness than wrough materials probably due to cold work hardening during plastic deformation**

**W. Y. Li and C. J. Li, ITSC2005**
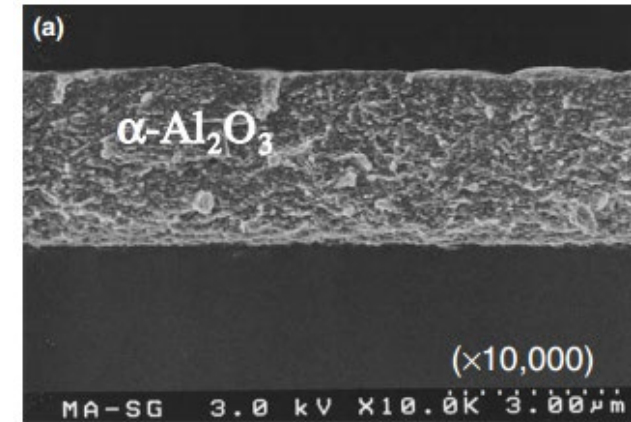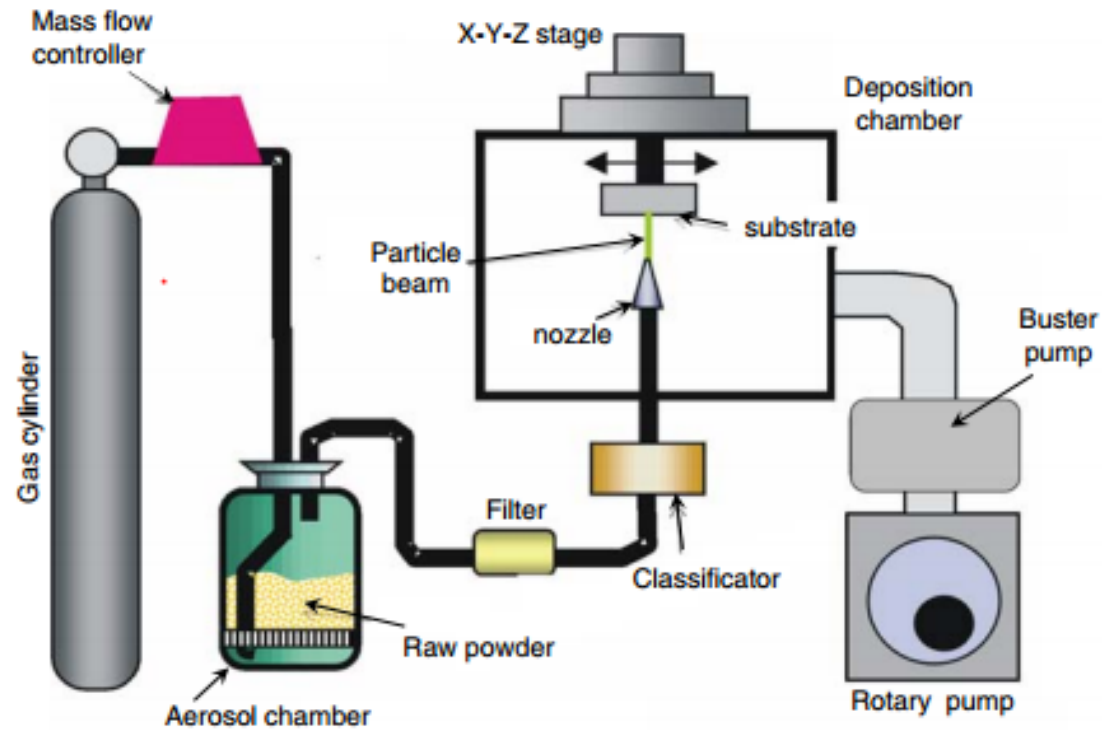
# Vacuum Cold Spray – Aerosol Spray





**Table 2   Mechanical properties of as-deposited AD layers**

| Material | Hardness (Hv) | | Average crystallite size of the layer (nm) | Particle velocity at the collision (m/s) |
| | Layer (deposited at R.T.) | Bulk (a) | | |
| --- | --- | --- | --- | --- |
| *Oxide* | | | | |
| A-Al$_2$O$_3$ | 1200-2100 | 1900 ± 100 | 13-20 | 150-500 |
| PZT | 400-550 | 350 ± 50 | 10-30 | 100-300 |
| (Ni,Zn)Fe$_2$O$_3$ | 700-750 | 1040 ± 80 | 5-20 | 250-600 |
| *Non-oxide* | | | | |
| AlN | 1100-1470 | 1180 ± 90 | 5-15 | 200-600 |
| MgB$_2$ | 700 | ... | 5-20 | 300-550 |

(a) Bulk sample were prepared from the same starting powder as layers, by conventional sintering procedure (at temperature over 1200 °C)
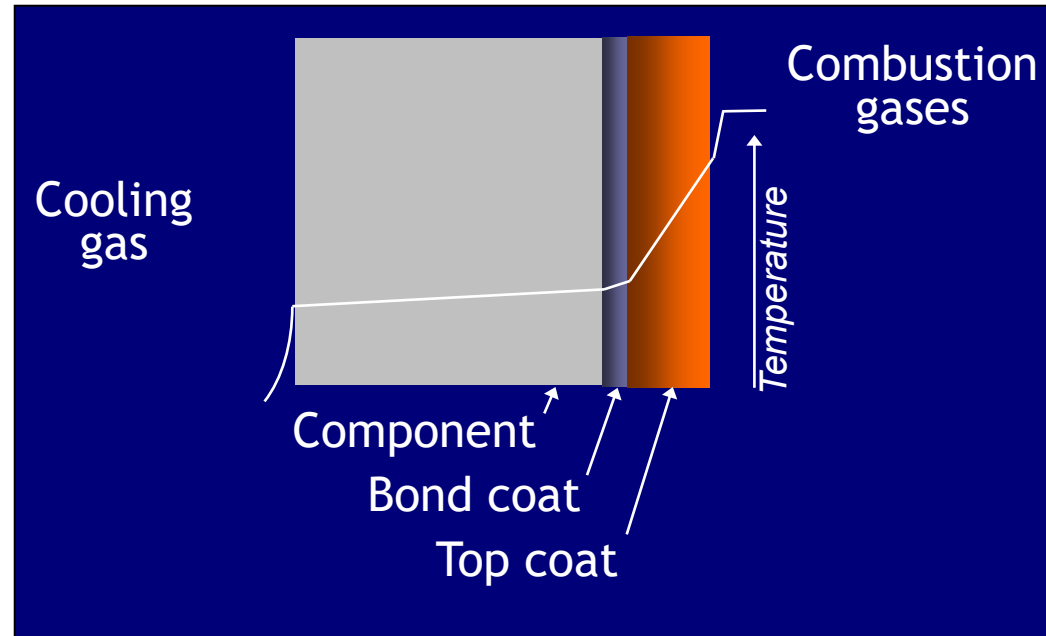
J. Akedo, JTST, 17 (2008) 181-198

# Applications

# Aerospace Applications
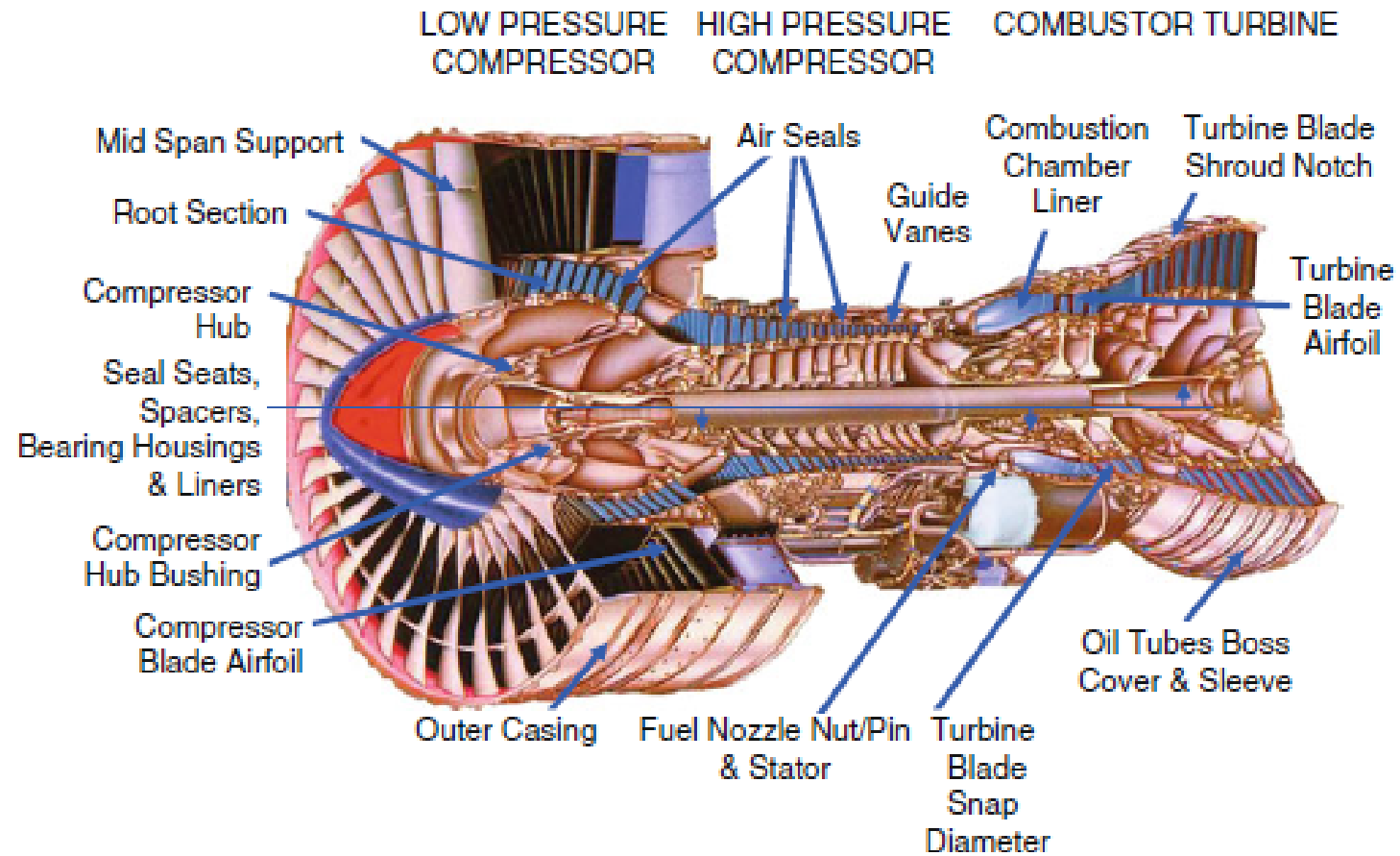


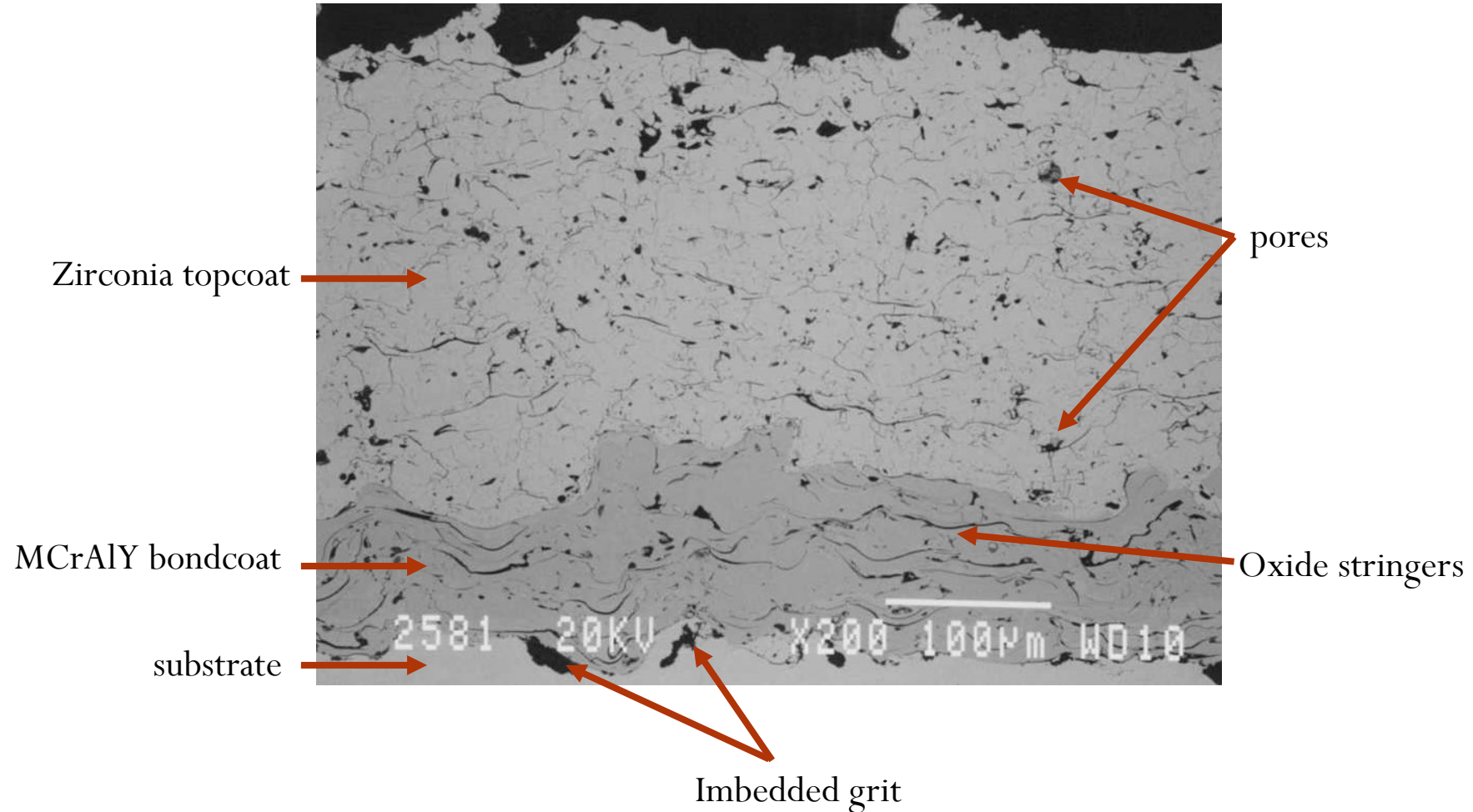*Walser B (2003), Spraytime 10(4) pp 1-7

# Thermal Barrier Coatings
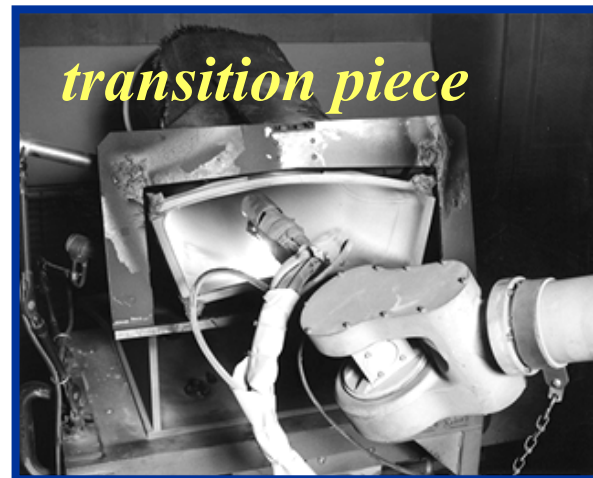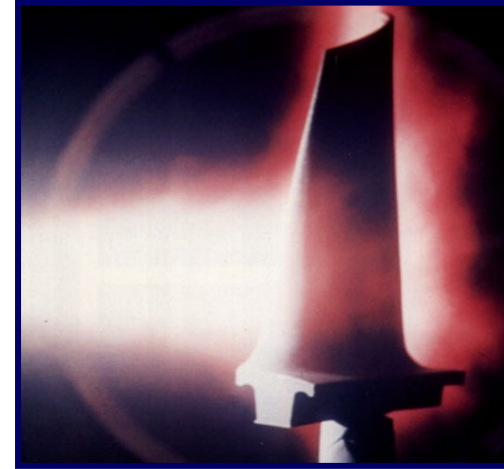
- Bond coat
    - MCrAlY
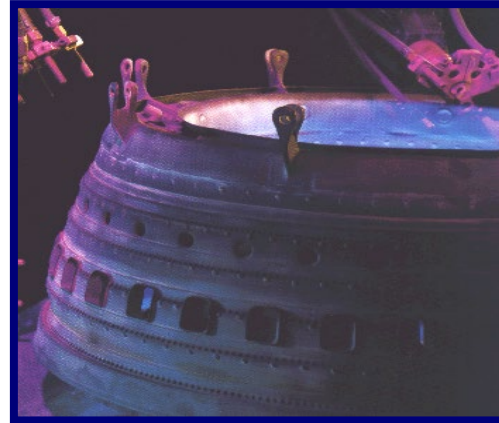- Top coat
    - Y-Stabilized ZrO2



- Main function: Protect the underlying component from high temperature gases

- Operating temperature (TBC surface): Up to ~1200°C $\Rightarrow$ temperature drop of up to ~150°C

# Thermal Barrier Coating System



Zirconia topcoat

pores

MCrAlY bondcoat

Oxide stringers

substrate

Imbedded grit

# Thermal Barrier Coatings



transition piece

combustion liner

*Courtesy of General Electric*
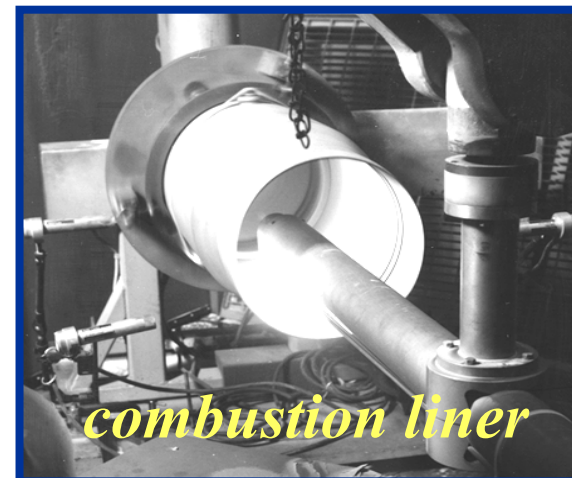
*Courtesy of Praxair Tafa*
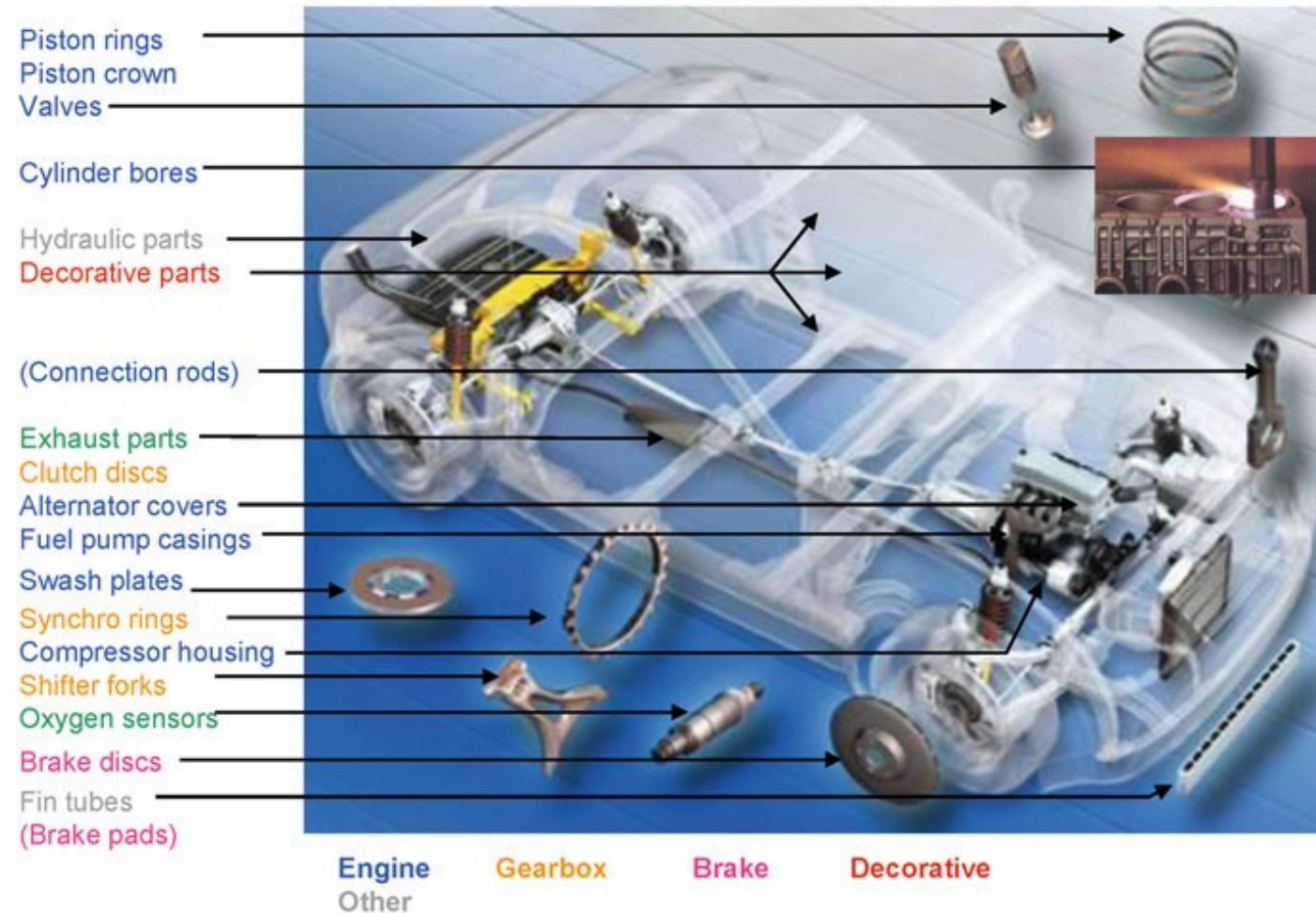
# Plasma Spraying: Internal Surfaces



Applications:
- Combustion chamber, transition ducts in gas turbines
- Cylinders bores of ICE Al blocks
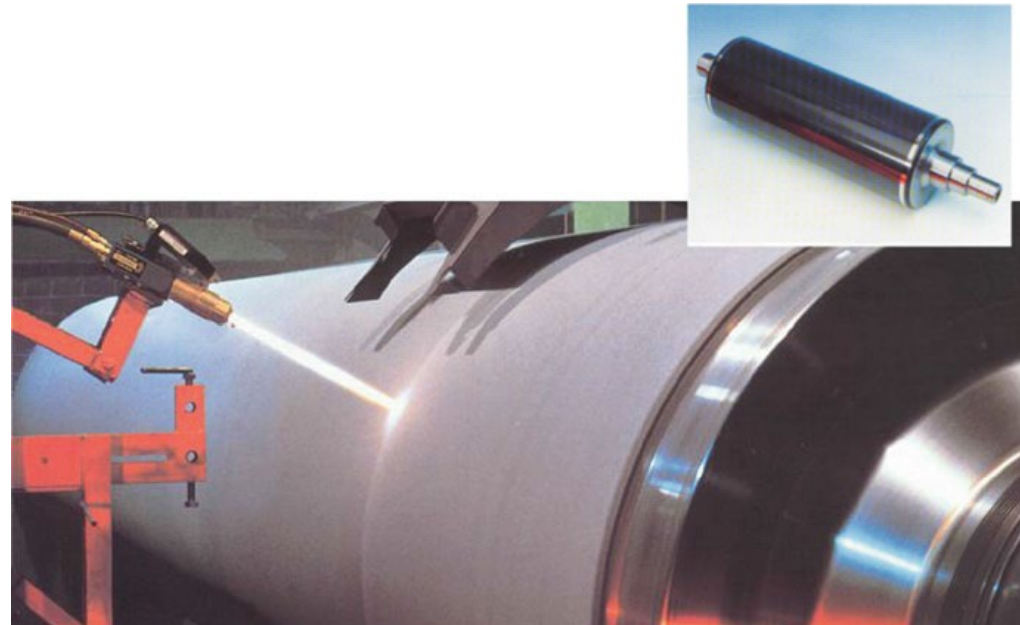
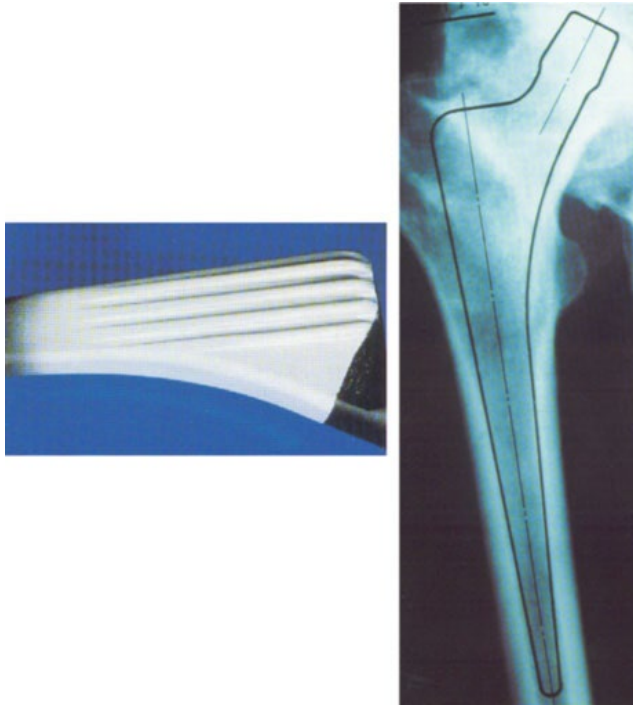Video courtesy of NRC Canada

# Automotive Applications



*Walser B (2003), Spraytime 10(4) pp 1-7

# Pulp and Paper

- Coatings applied for wear and corrosion protection



Thermal Spray Fundamentals, Fauchais et al., 2014

# Biomedical Applications



- Thermal spray hydroxyapatite (HA) coatings for improved bone adhesion for hip and dental implants

- HA is the main inorganic bone constituent

Thermal Spray Fundamentals, Fauchais et al., 2014

# Solid Oxide Fuel Cell



Solid Oxide Fuel Cell

http://electrical-engineering-portal.com/getting-electricity-from-solid-oxide-fuel-cell

➢ **Highly efficient devices to convert chemical energy into electrical energy and heat with low environmental impact**
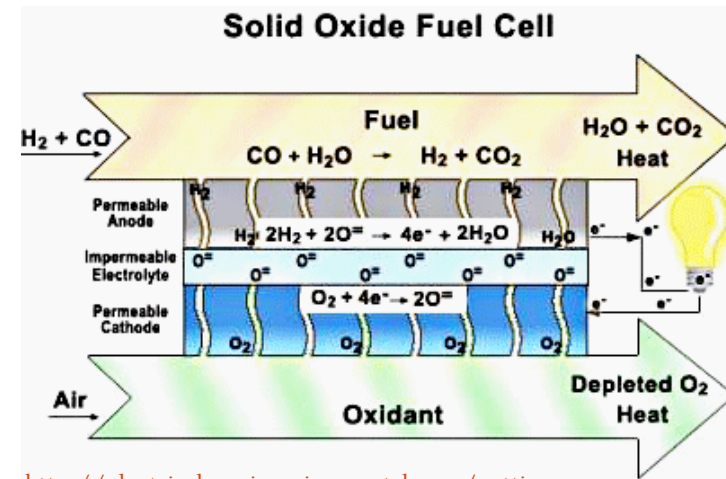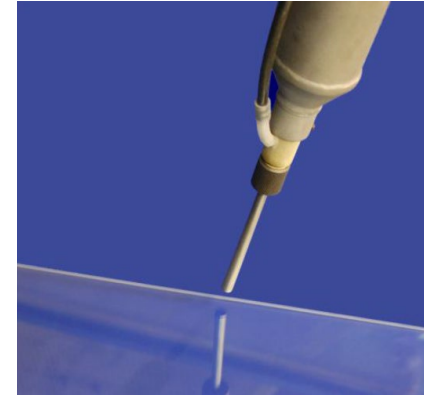
**Reduction of component and overall manufacturing cost for next-generation Solid Oxide Fuel Cells (SOFC).**



*Images courtesy of NRC Canada

109
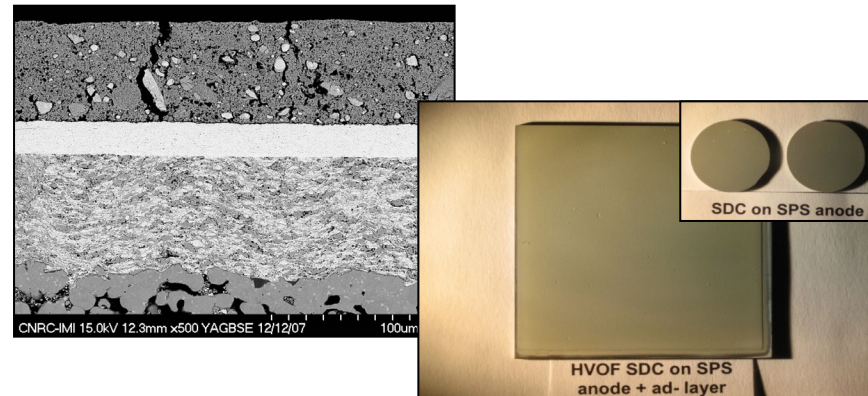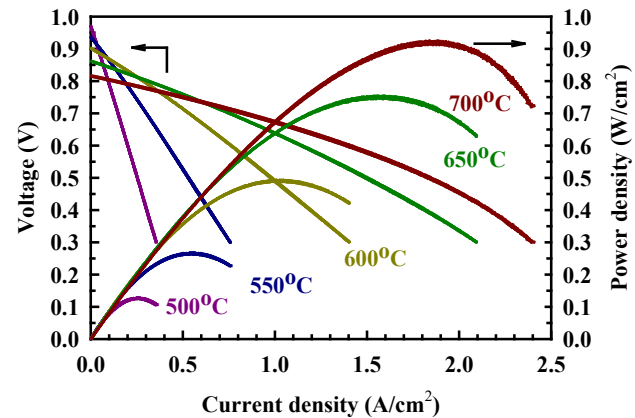
# Cold Spray Applications

- Coatings for wear, corrosion and oxidation protection
- Repair (magnesium components)
- Additive manufacturing
  - 2D printing (busbars on tin oxide coated glass)
  - 3D manufacturing



Current Trends in Cold Spray Technology: Looking at the Future in Metal finishing.com; 8 Jan 2010



Heat Exchangers: Brayton Energy Canada

# Final Comments

- Thermal spray processes are used intensively in the industry and the market is rapidly growing

- Spray materials have unique properties that can be tailored according to the targeted application

- Innovative processes, such as suspension plasma spray and cold spray, are in active development and stimulate important research efforts for new high performance coatings and new applications