Le nuove frontiere delle tecnologie al plasma - Esempi di applicazioni industriali

Consorzio Innova FVG - 24 Settembre 2018

Thermal Spray Coatings For Industrial Applications

SAPIENZA
UNIVERSITÀ DI ROMA

INSTM - Italian Consortium on Materials Science and Technology

Giovanni Pulci

INSTM Research Unit "Roma La Sapienza"

Dept. of Chemical and Materials Engineering (ICMA)

Sapienza University of Rome

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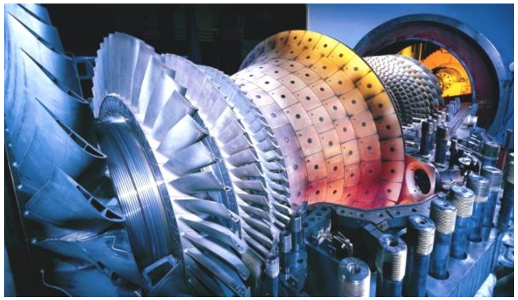
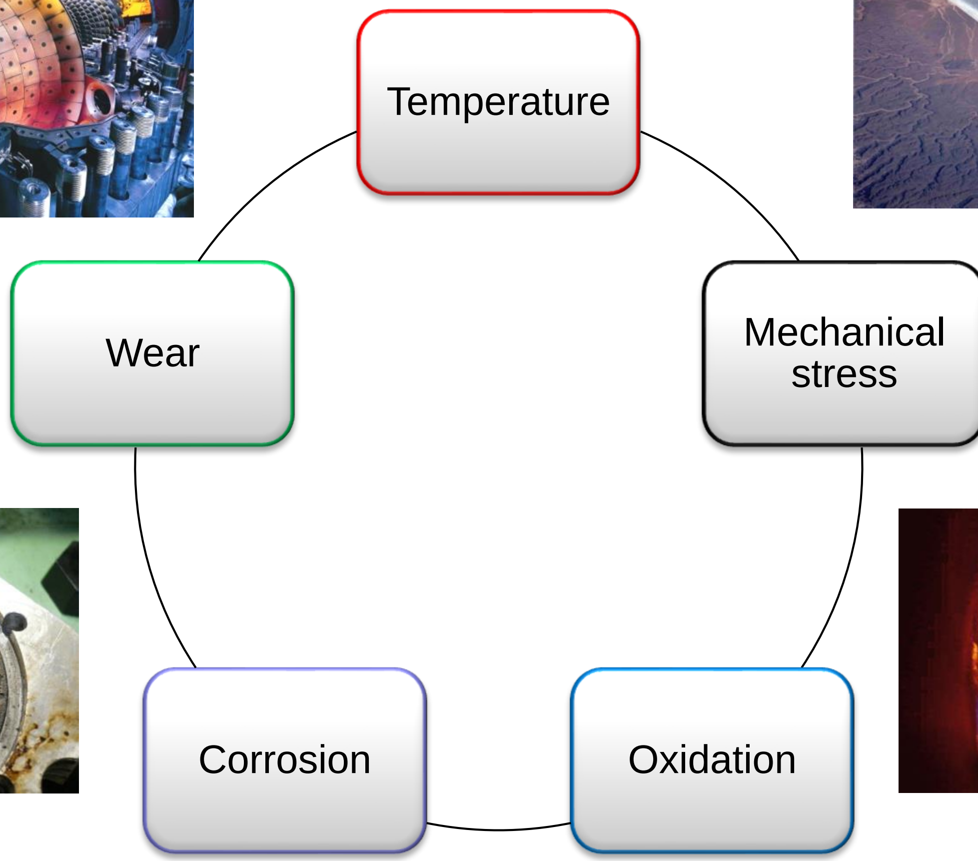
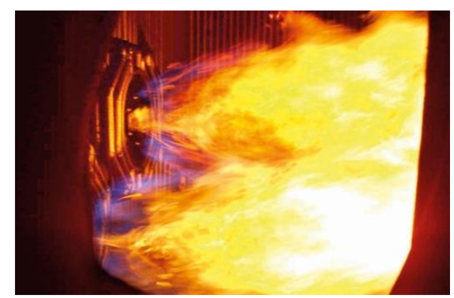
Coatings for severe operating environment

Heavy combination of mechanical stresses and aggressive environment

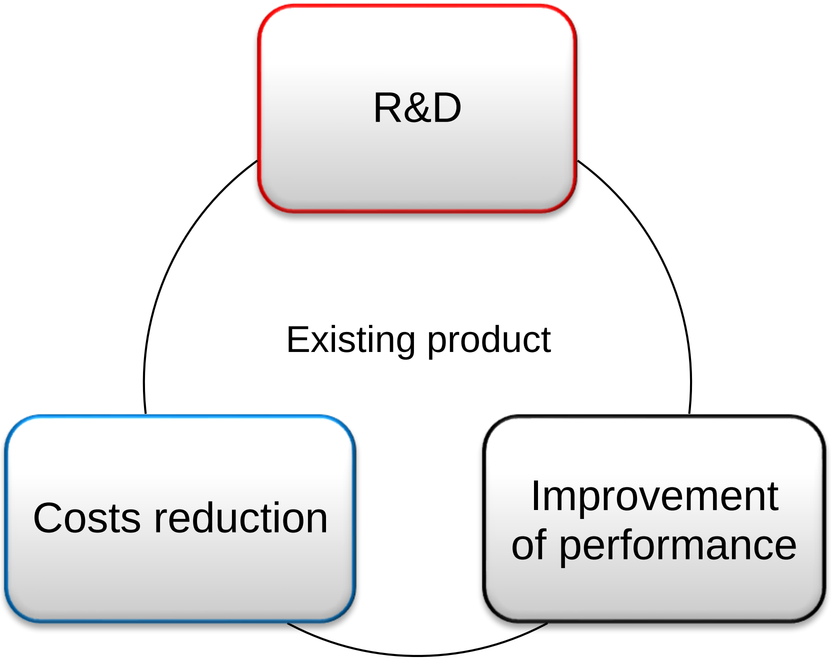


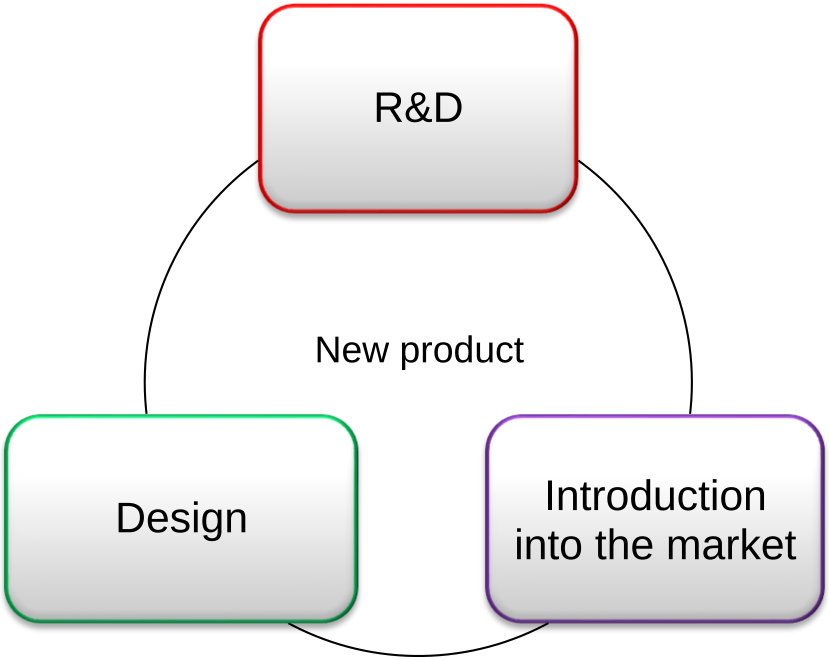




Coatings for severe operating environment

R&D plays a key role for component working in critical operating conditions





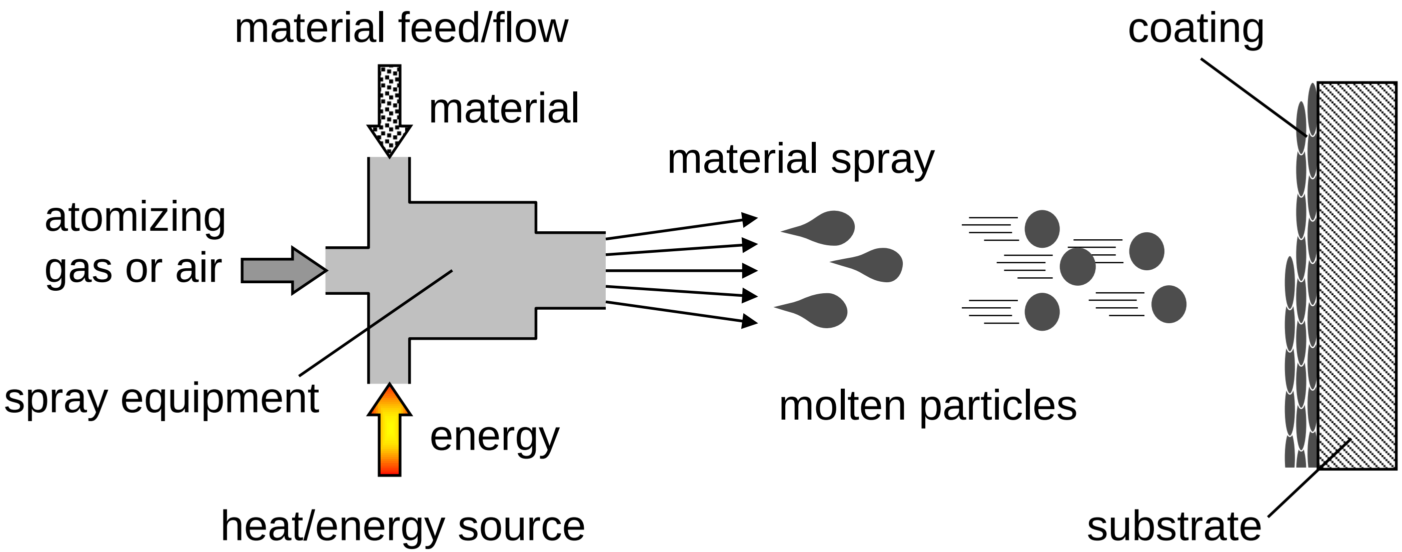
Aim of presentation:

Description of case studies related to innovations and R&D in thermal spray field

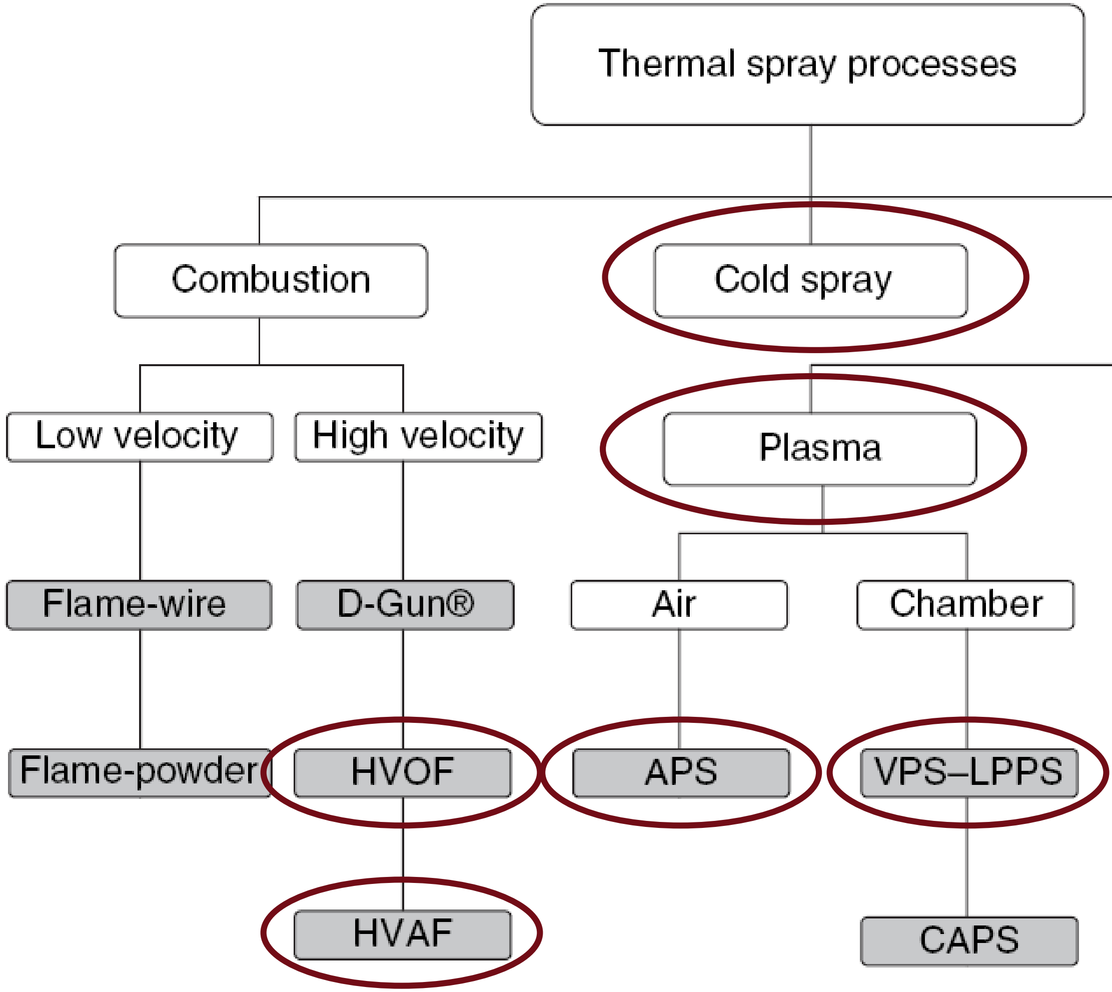
Surface engineering by thermal spray process

A thermal spray process can be divided into four sections:

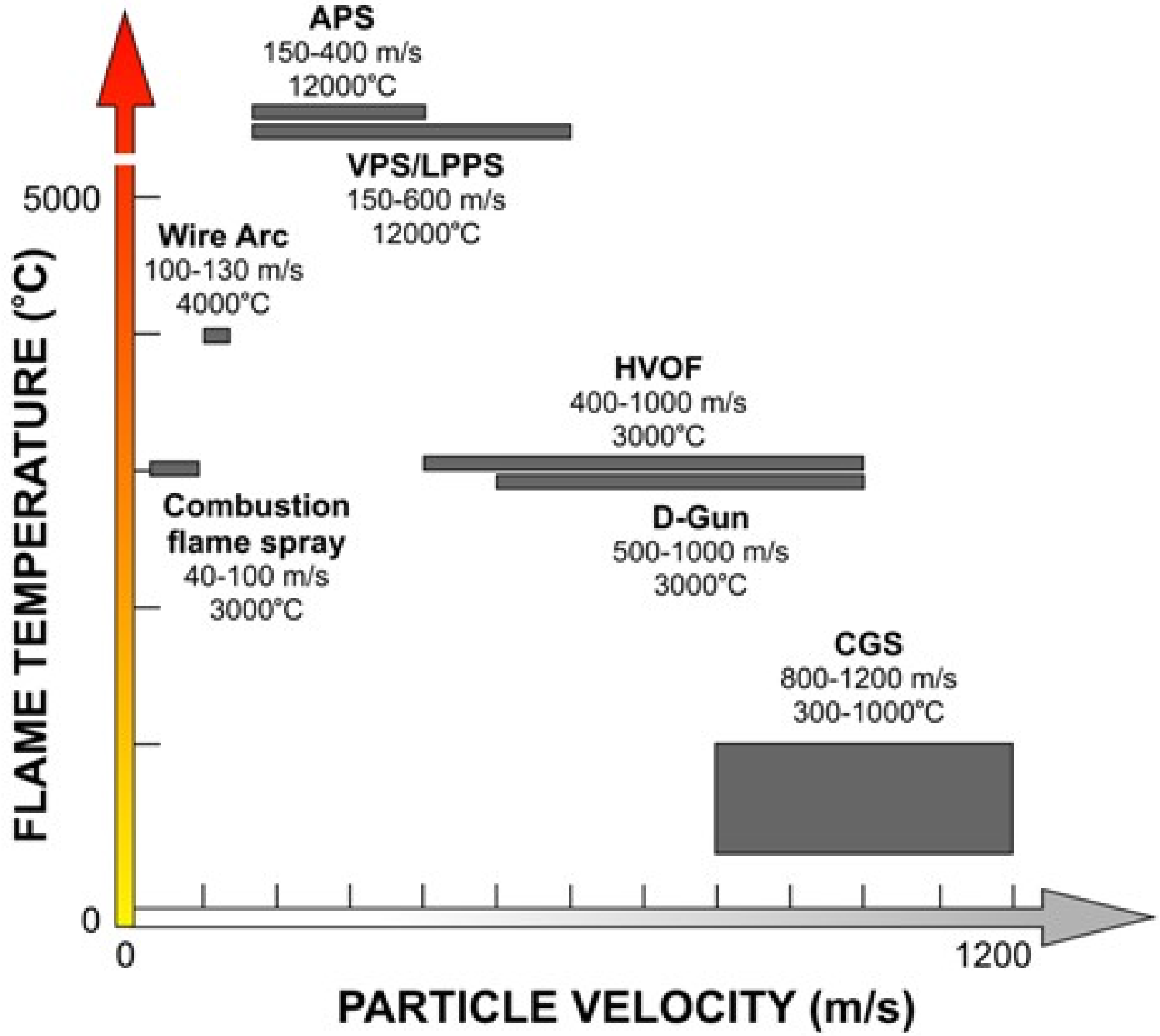
- heat/energy source (thermal energy for heating and melting)
- material feed/flow
- material spray (kinetic energy for propelling dispersion)
- material deposition



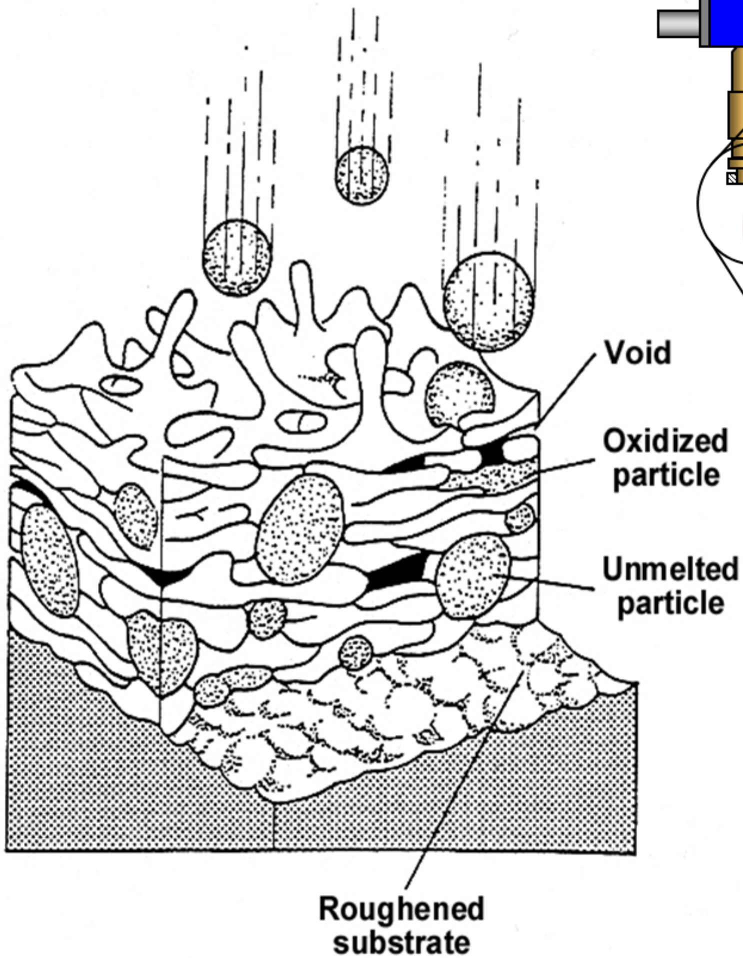
Surface engineering by thermal spray processes

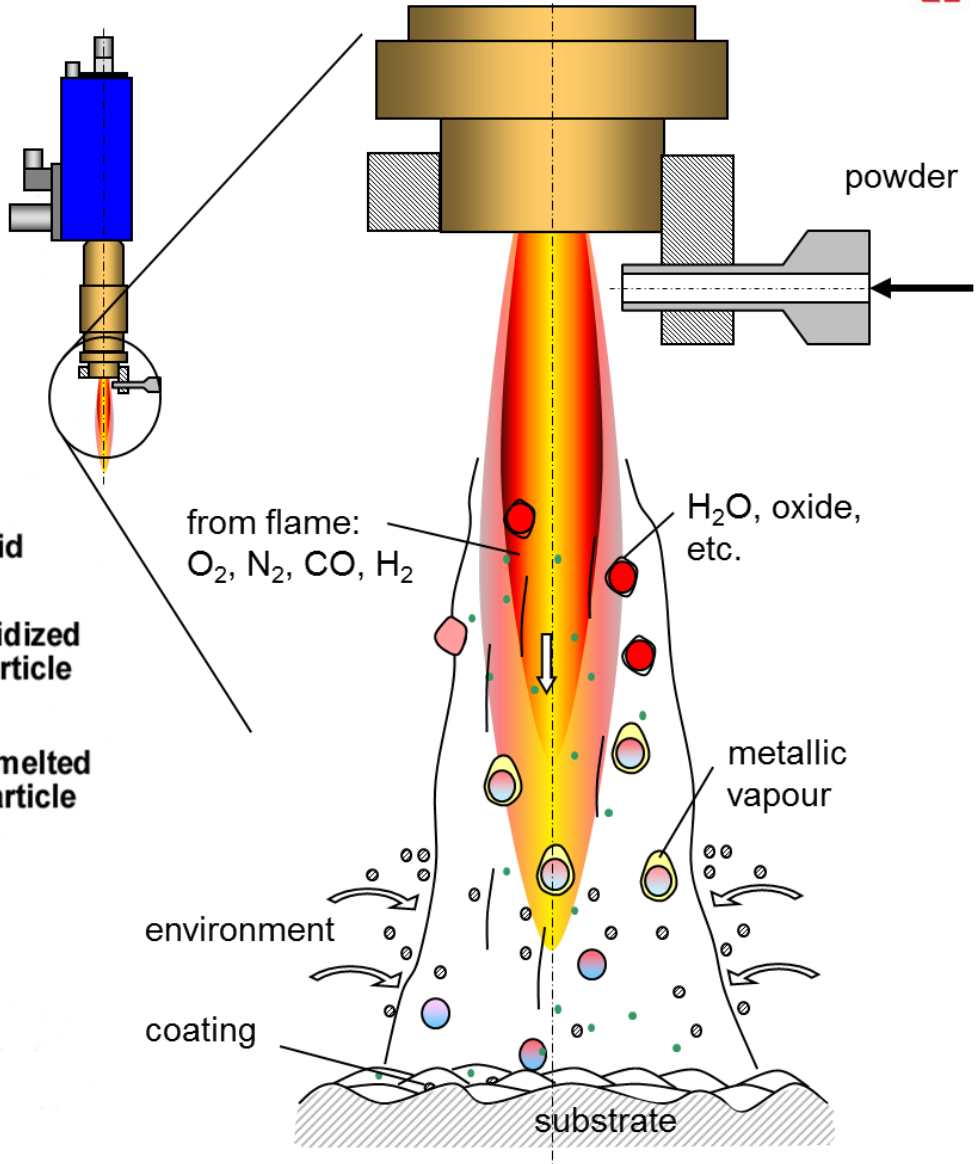


Surface engineering by thermal spray processes

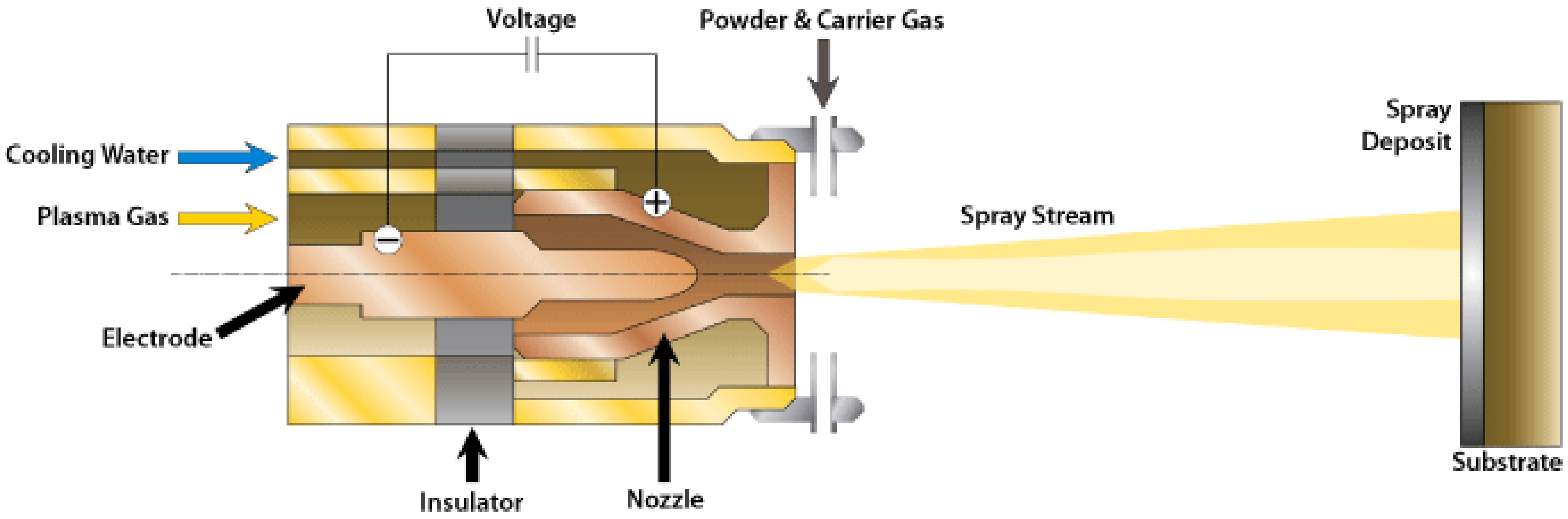


Coating formation



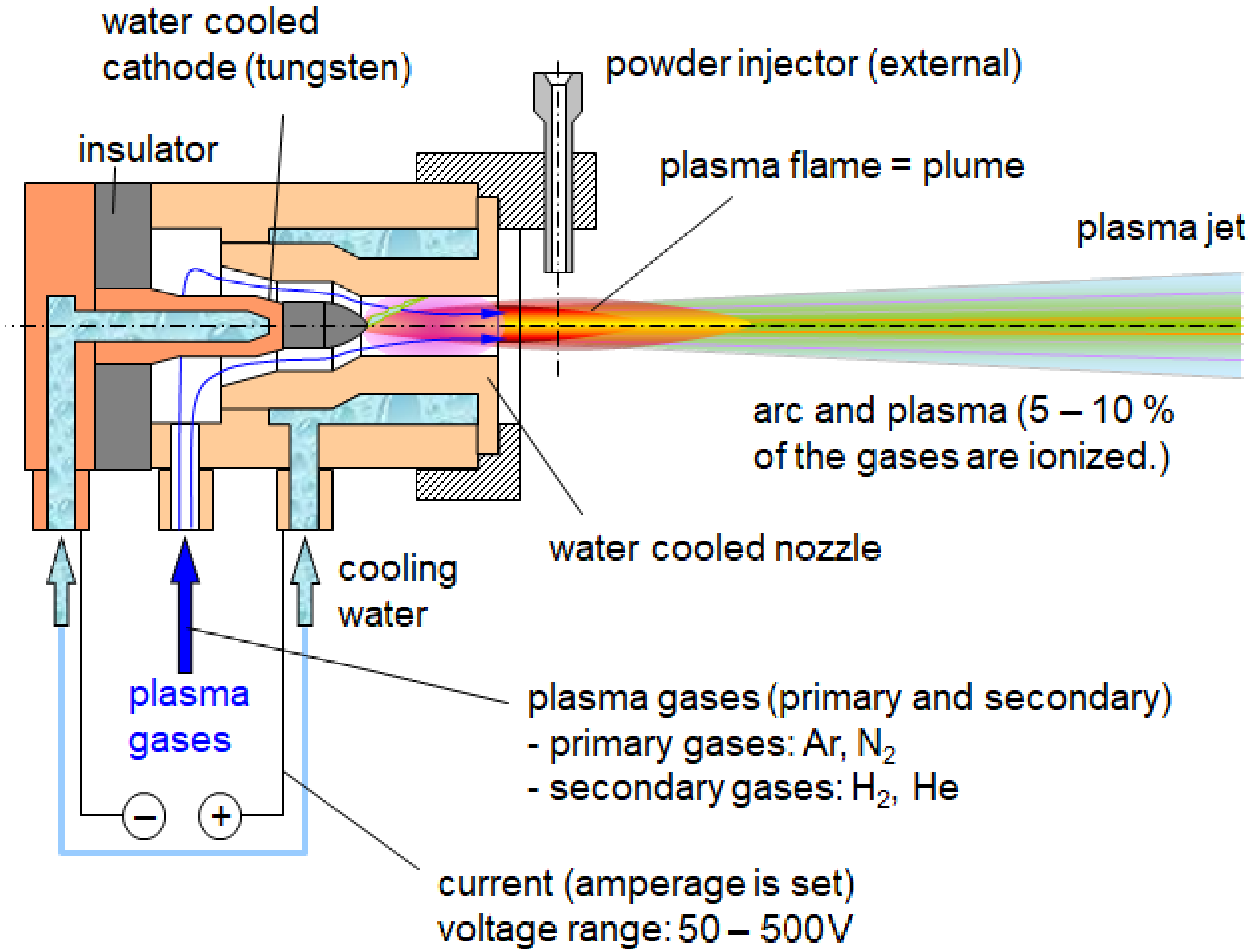


Plasma spraying

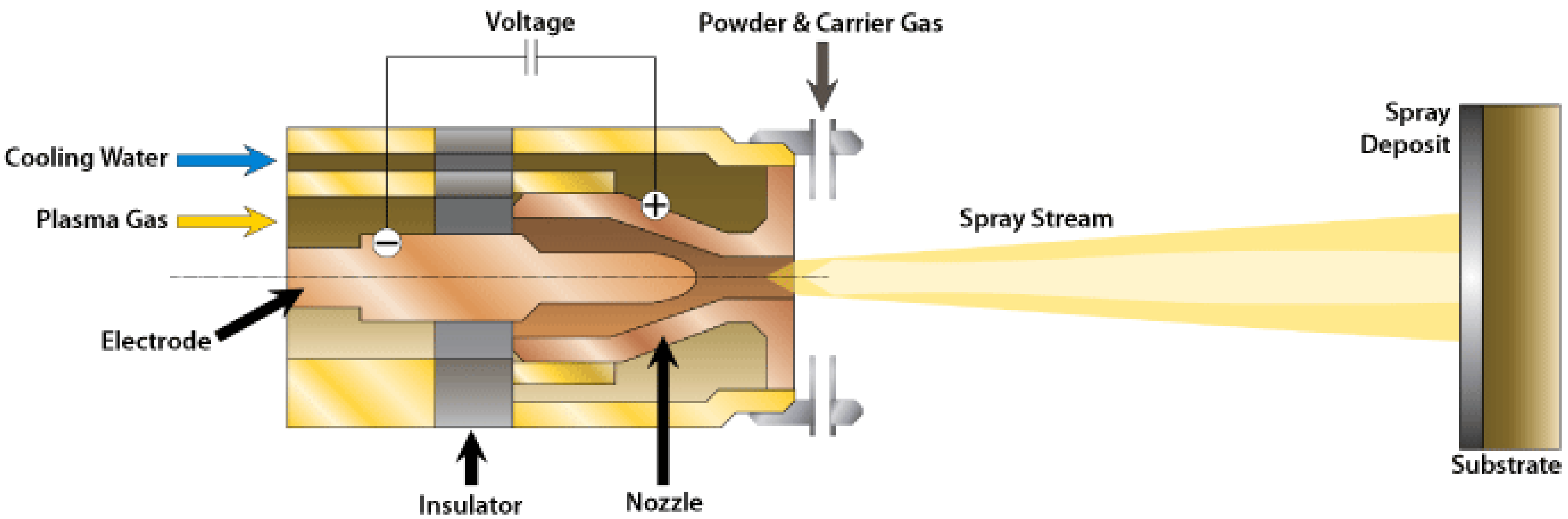


- An inert gas is passed through a potential differential.
- An arc is formed between the two dipoles.
- The gas is ionized and recombines after going through a free expansion.
- The recombination effect releases heat and creates a plasma flame ("plume").
- Powder is inserted into the flame and is propelled towards the substrate.

Plasma spraying



Plasma spraying

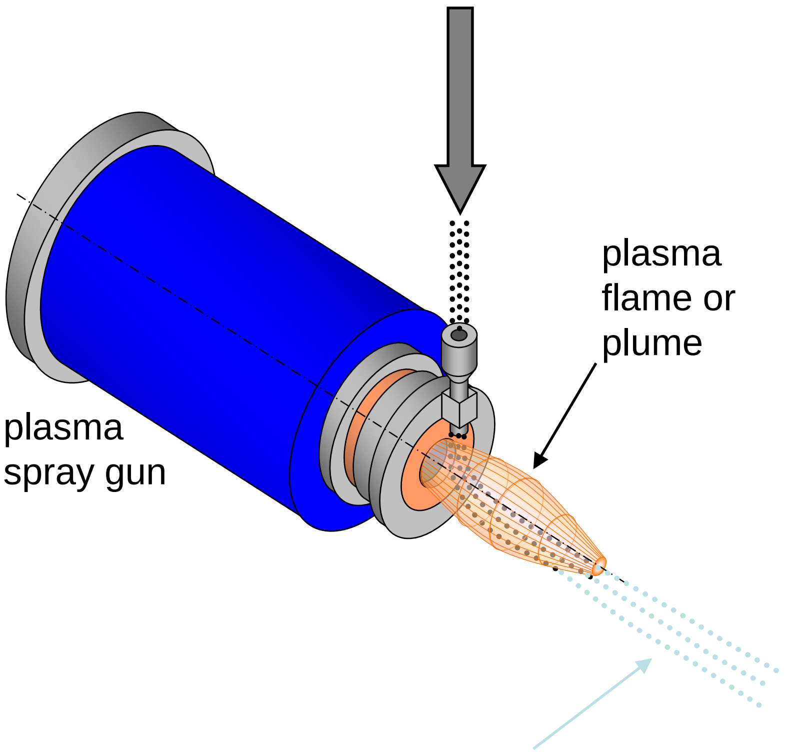


- **Max. plume temperature** **≈ 12000 ° C**
- **Impact speed of particles** **200-400 m/s**
- **In-flight time of particles** **≈ 10^{-3} s**
- **Heating/cooling rate** **≈ 10^{7} K/s**

Plasma spraying

Process parameters

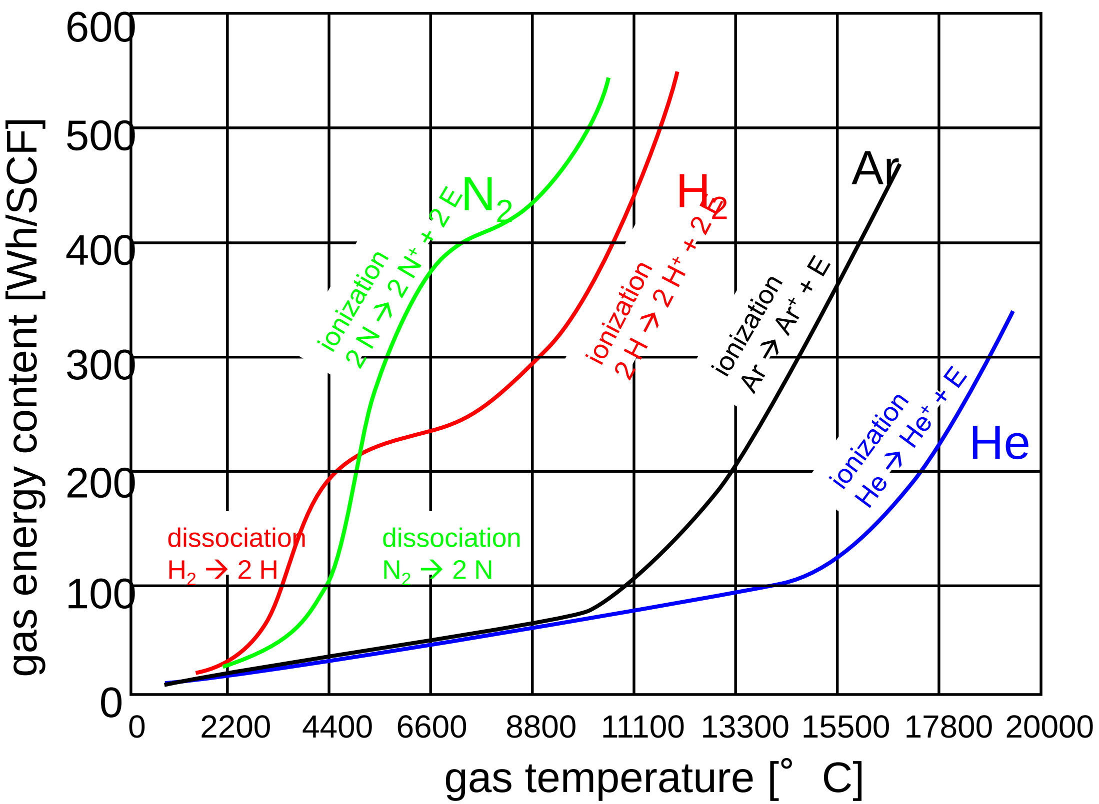
- Plasma (Primary) gas flow
- Secondary gas flow
- Plasma power
- Spray distance
- Injector angle, length and size
- Carrier gas flow
- Gun spray angle



Plasma spraying

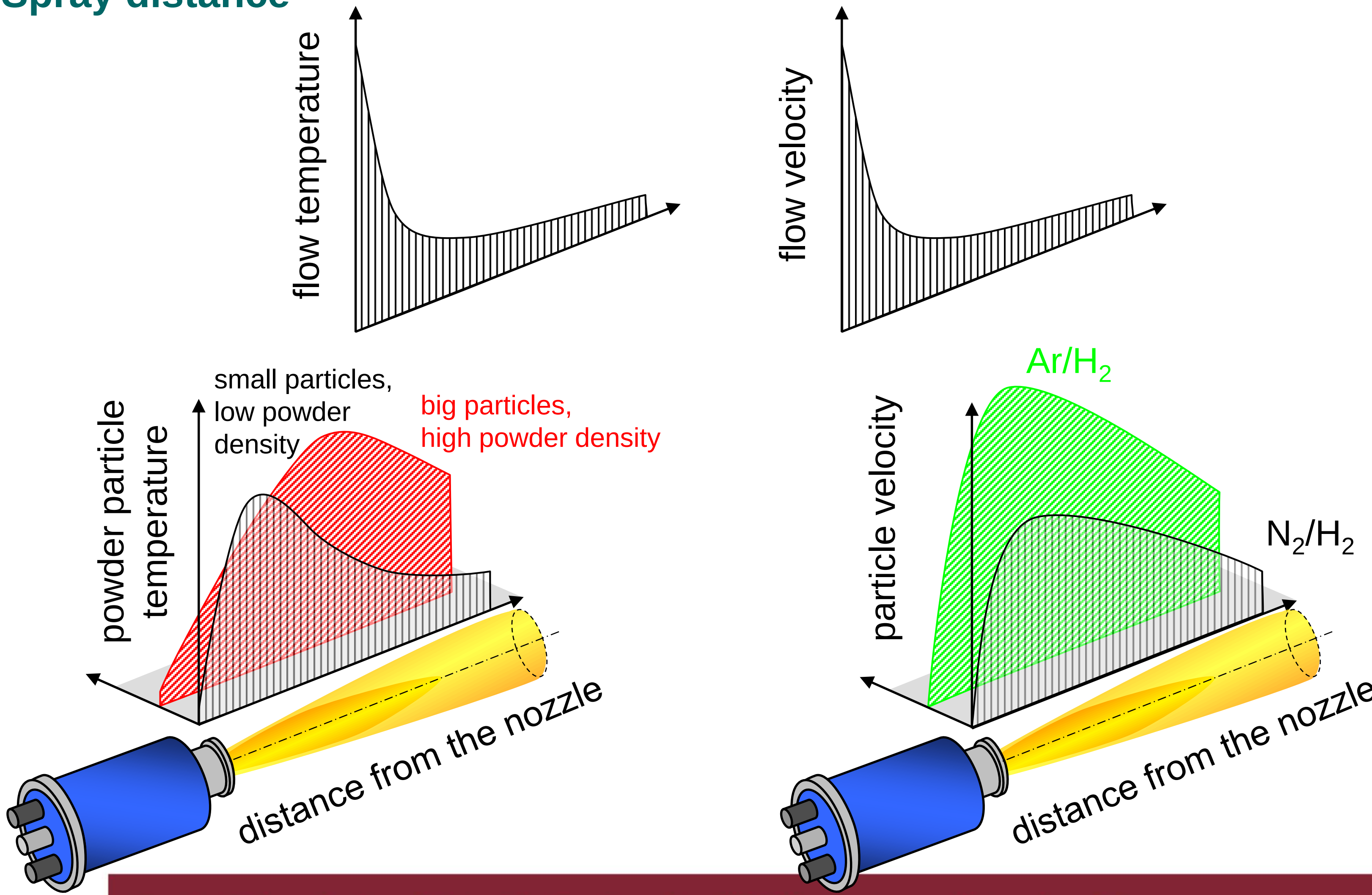
Plasma gases

- Primary gases (Ar, N_2): plasma stability and transport properties
- Secondary lighter gases (He, H_2), enthalpy adjustment.
- N_2 and H_2 are diatomic gases. These plasmas have higher energy contents for a given temperature than argon and helium because of the energy associated with dissociation of molecules.



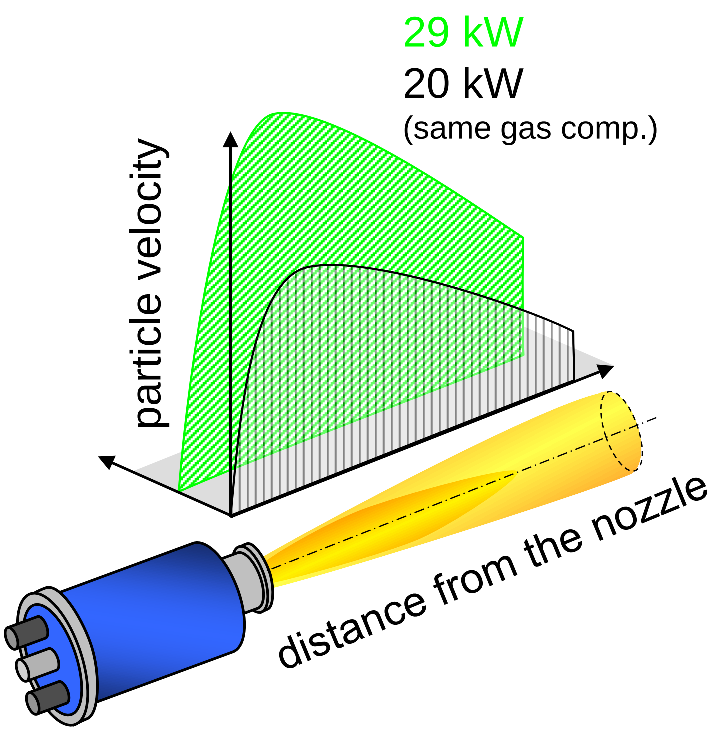
Plasma spraying

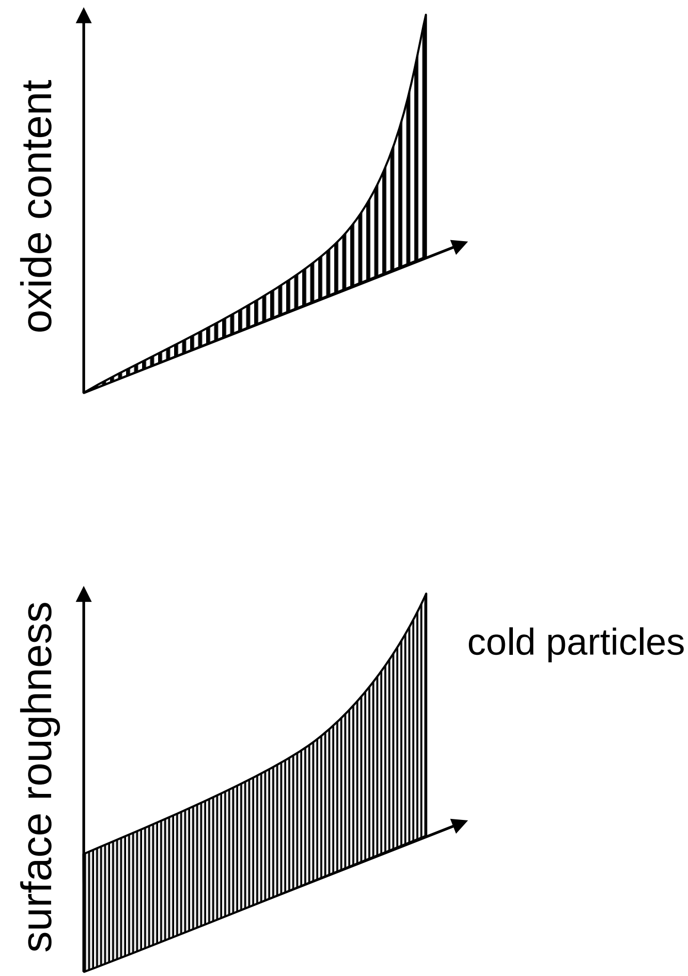
Spray distance



Plasma spraying

Spray distance





Plasma spraying

Controlled Atmosphere Plasma Spray

chamber is backfilled after evacuation, either at

- near vacuum (1 - 10 mbar) **VPS**
- reduced pressure (> 50 mbar) **LPPS**
- standard pressure **APS**
- elevated pressure (up to 4 bar) **HPPS**
- with a substitute atmosphere (reactive (CxHy), inert (Ar)) **RPS / IPS**

VPS / LPPS / LVPS

- spraying in near vacuum or under reduced pressure conditions
- spray particles are unimpeded by frictional forces of the atmosphere

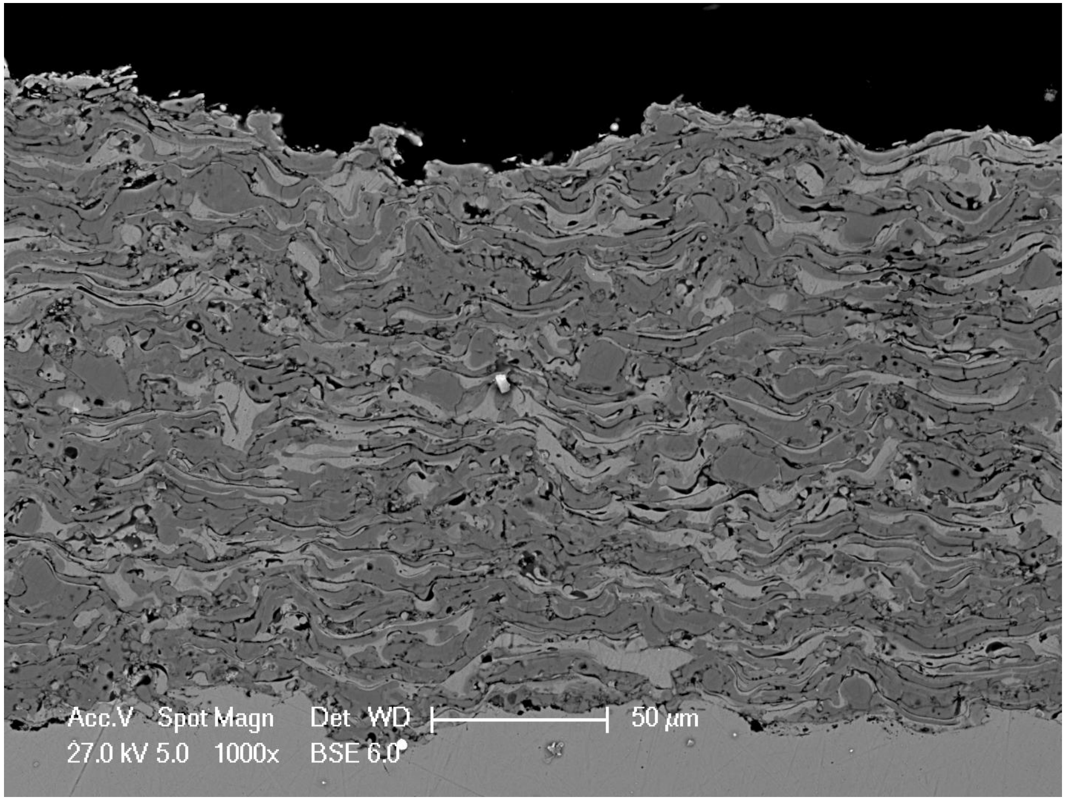
Plasma spraying

Materials

- Ceramics (high melting point)
    - Al_2O_3, Al_2O_3/TiO_2, Cr_2O_3, ZrO_2 -Y_2O_3, $La_2Zr_2O_7$, ecc.
    - ZrB_2, TiB_2, SiC (non standard)
- Metals (refractory, oxidation control is mandatory, controlled atmosphere)
    - MCrAlY, Ni-and Mo-based alloys
- Cermets
    - Cr_3C_2 - based (high T, generally NiCr matrix)
    - WC - based (better mechanical properties, T_{max} 500 ° C (decarburation), Co - CoNiCr - based matrix)

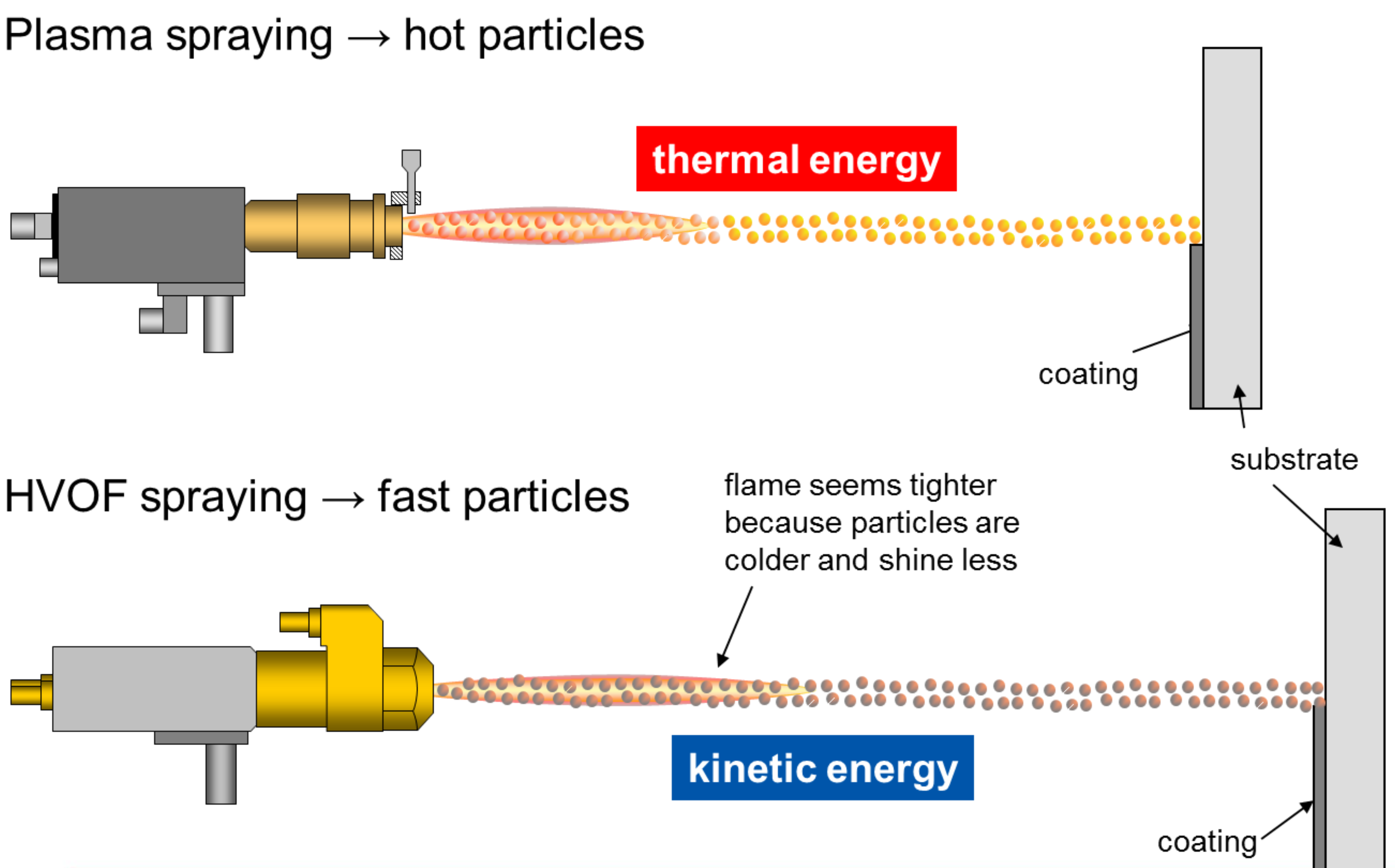
Plasma spraying

Cermet Cr_3C_2 – Ni-Cr



- Low porosity
- Lamellar microstructure, partially molten ceramic phase

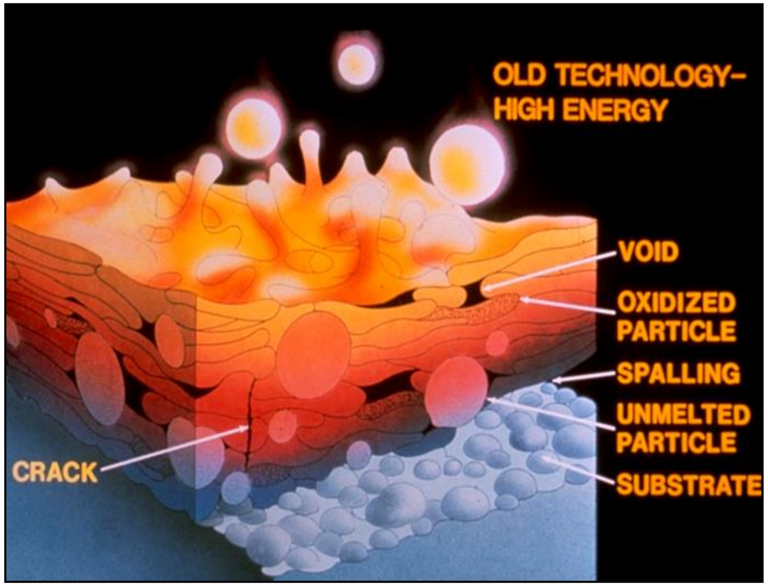
Coating formation – plasma vs. HVOF



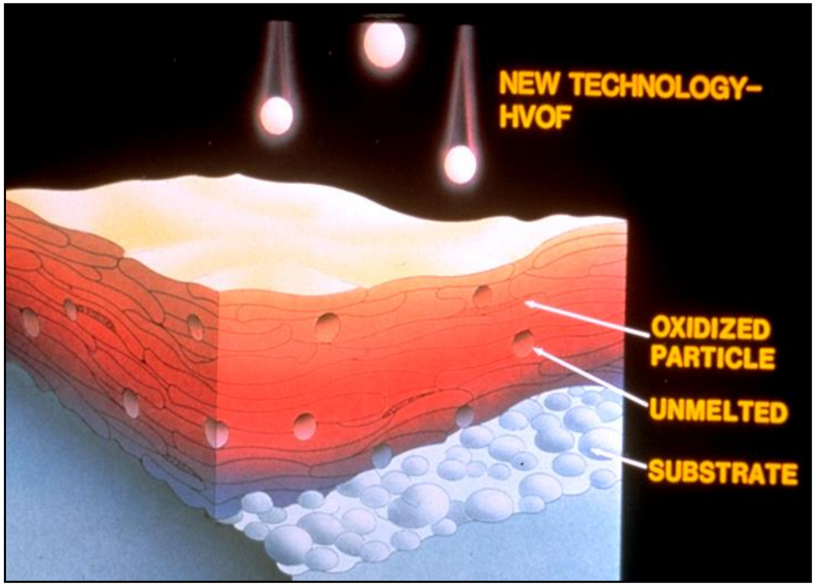
HVOF deposition

- **Max. jet temperature** ≈ 2800 ° C
- **Particles impact speed** 400-700 m/s
- **In-flight time** ≈ 10^{-3} s
- **Heating/cooling rate** ≈ 10^{7} K/s

Plasma Spray



HVOF



Applications

Wear and corrosion resistant coatings

(Mechanical, chemical, aerospace, textile industries)

- Cermet (WC, Cr_3C_2 or TiC in Co, Co-Cr or Ni-Cr metal matrix);
- Ceramics (Cr_2O_3, Al_2O_3-TiO_2);
- Metallic (Ni or Co base, e.g. NiCrBSiC).

Thermal barrier coatings (TBC)

(Aerospace, energy industries)

- ZrO_2 - Y_2O_3.

High temperature oxidation resistant coatings

(Aerospace, energy, chemical industries)

- Ni - Cr – Al base (e.g. NiCoCrAlY).

Biocompatible coatings

Porous Ti , hydroxy apatite $(Ca_{10}(PO_4)6(OH)_2$

Materials and Surface Engineering Lab

Research partners and clients

AIRBUS DEFENCE & SPACE

GE Oil & Gas Nuovo Pignone spa

WÄRTSILÄ

asi agenzia spaziale italiana

ThalesAlenia Space A Thales / Finmeccanica Company

CIRA

ANSV

Avio Aero A GE Aviation Business

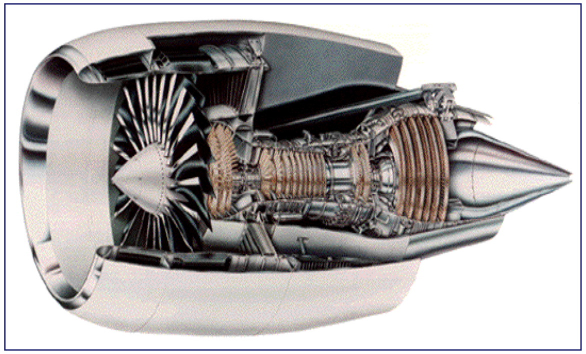
aviospace

esa

MBDA MISSILE SYSTEMS

AVIO

Aircraft engines and power gas turbines

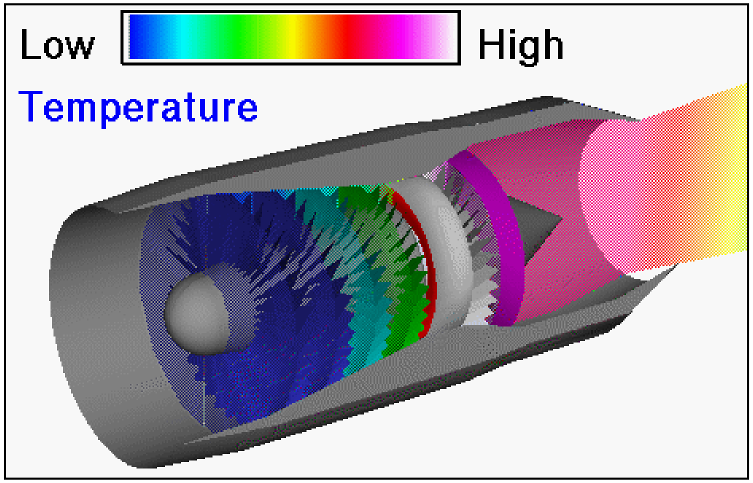


Max gas temperature in turbine:
900 - 1400 ° C

Rise in gas temperature in turbine

↓

Improvement of thermodynamic efficiency



Turbine blades protection

High temperature and combustion products (e.g. SO_2, SO_3, V_2O_5) cause surface damages on the Ni-base superalloy

Hot corrosion
(700 – 925 °C)
(SO_3 attack, sulphides formation)

High temperature oxidation
(T > 1000° C)

Erosion
(Solid particles in gas stream)

Max service temperature of superalloy!

Protective ceramic overlay

Thermal Barrier Coating (TBC)

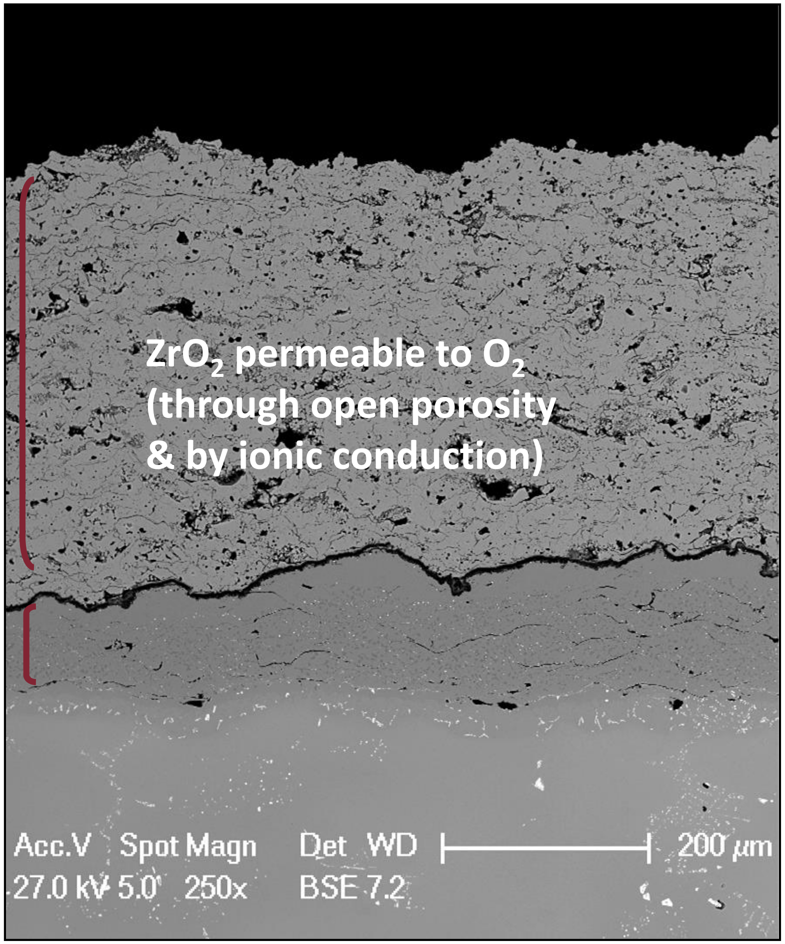
Thermal Barrier Coatings (TBC)

Top Coat (ZrO_2–6-8%Y_2O_3)

TGO (a-Al_2O_3)

Bond Coat (Ni/Co-CrAlY)

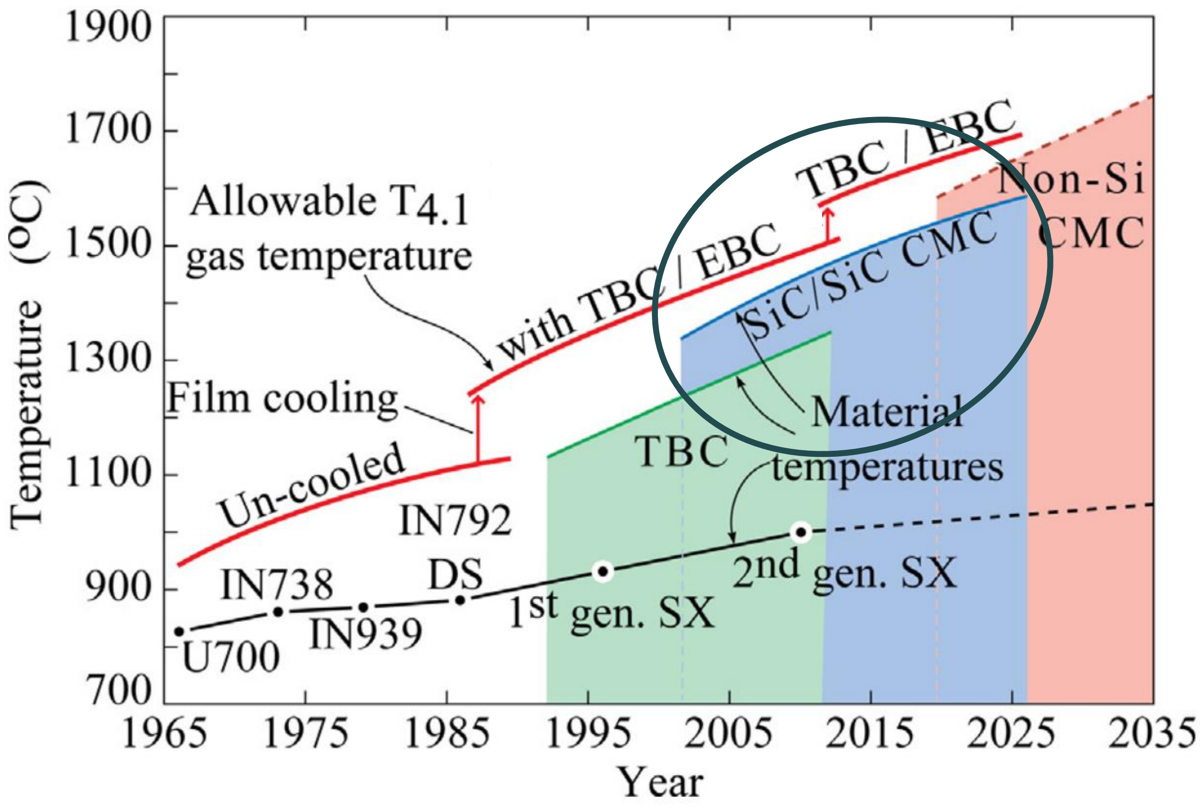
Substrate (Ni–base superalloy)



- Thermal insulation
- Erosion protection
- Oxidation barrier
- Enhanced adhesion
- Hot corrosion resistance
- Thermo-mechanical loading

Innovative materials for gas turbines

Strategies to improve turbines performance: use of CMC materials



Innovative materials for gas turbines

Strategies to improve turbines performance: use of CMC materials

Modification of substrate-coating system

(12) **United States Patent**
Subramanian et al.

(10) **Patent No.:** **US 8,114,799 B2**
(45) **Date of Patent:** **Feb. 14, 2012**

(54) **FUNCTIONALLY GRADIENT SIC/SIC CERAMIC MATRIX COMPOSITES WITH TAILORED PROPERTIES FOR TURBINE ENGINE APPLICATIONS**

(75) Inventors: **Suresh Subramanian**, Mason, OH (US); **James Steibel**, Mason, OH (US); **Douglas Carper**, Trenton, OH (US); **Toby Darkins, Jr.**, Loveland, OH (US)

(73) Assignee: **General Electric Company**, Schenectady, NY (US)

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Innovative materials for gas turbines

Strategies to improve turbines performance: use of CMC materials

Modification of substrate-coating system

GE Rolls-Royce – development of F136 engine (second choice for F-35 aircraft)
3rd low pressure stage – stator in SiC/SiC

Innovative materials for gas turbines

Strategies to improve turbines performance: use of CMC materials

Modification of substrate-coating system

GE Aviation

GE Successfully Tests World's First Rotating Ceramic Matrix Composite Material for Next-Gen Combat Engine

F414 low-pressure turbine blades prove silicon carbide CMC material for unprecedented deployment in GE's adaptive cycle combat engine

February 10, 2015

CINCINNATI, OH – February 10, 2015 – GE Aviation successfully tested the world's first non-static set of light-weight, ceramic matrix composite (CMC) parts by running rotating low-pressure turbine blades in a F414 turbofan demonstrator engine designed to further validate the heat-resistant material for high-stress operation in GE's next-generation Adaptive Engine Technology Demonstrator (AETD) program currently in development with the United States Air Force Research Lab (AFRL).

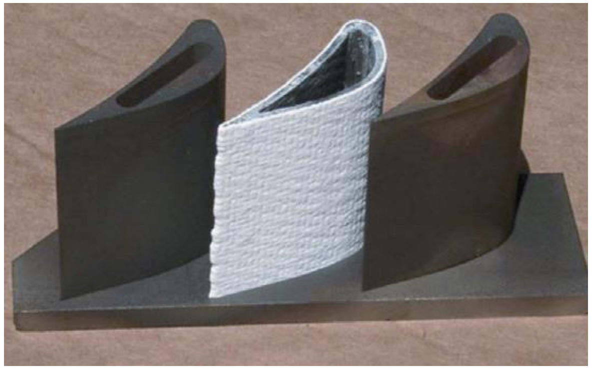
Innovative materials for gas turbines

Strategies to improve turbines performance: use of CMC materials

Modification of substrate-coating system

Problem:

- Active oxidation of SiC/SiC, expecially in presence of H_2O steam: *Thermal & Environmental Barrier Coatings*

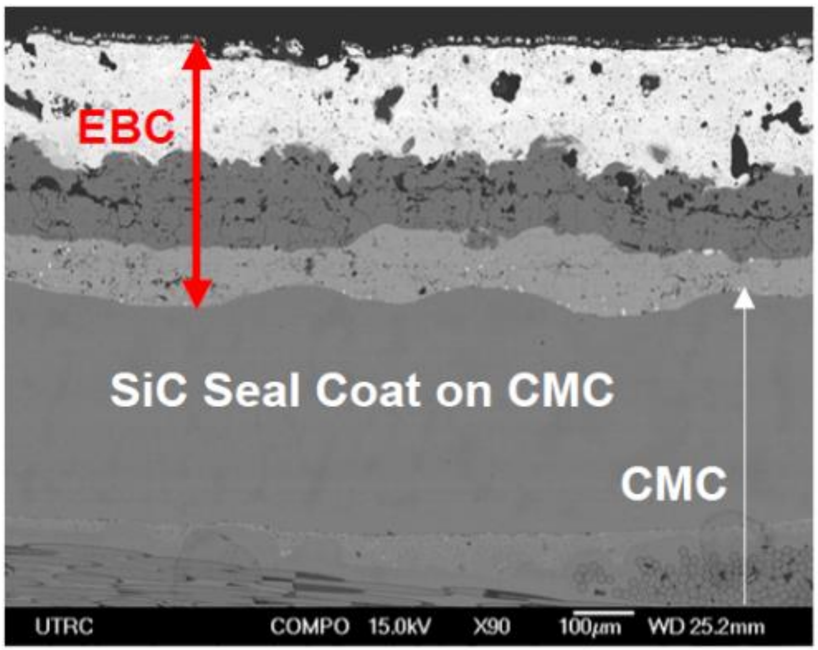


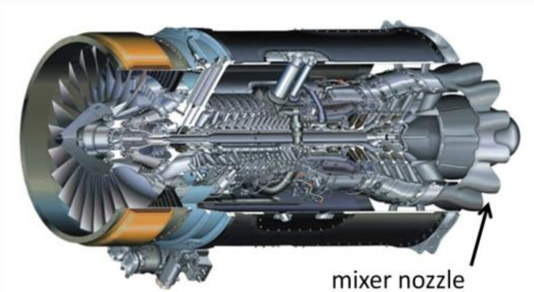
Innovative materials for gas turbines

Environmental Barrier Coatings

EBC deposited by APS (examples)

- HfO_2-Y_2O_3-Gd_2O_3-Yb_2O_3
- Barium-Strontium-Alumino-Silicate (BSAS)





CMC shroud for 7F fleet helps increase GT output, reduce heat

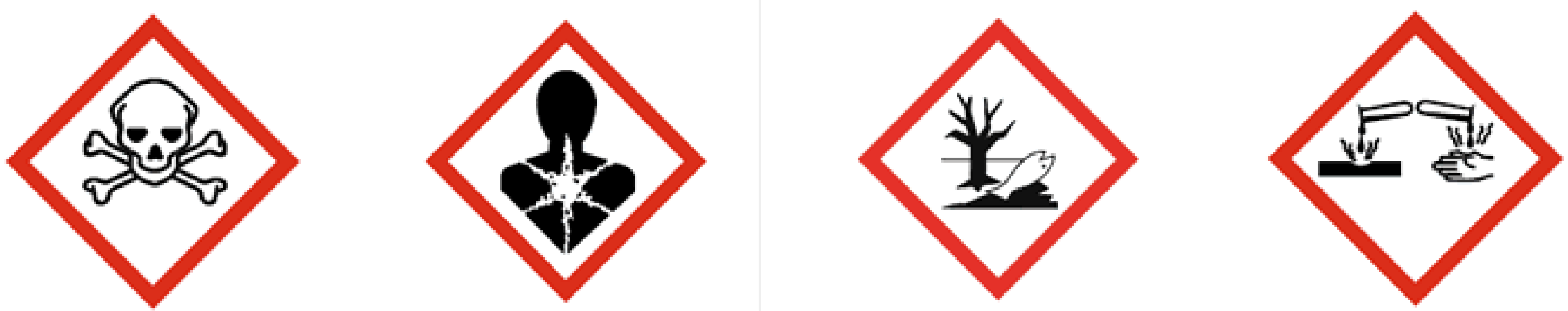
Need for innovation in surface engineering

Case study: Hard chrome replacement

Hard Chrome plating is an electrolytic method of depositing chrome for engineering applications, from a chromic acid solution.

Cr^{6+} compounds

EU classification



COMMISSION REGULATION (EU) No 348/2013

of 17 April 2013

amending Annex XIV to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

Substance	Intrinsic property(ies) referred to in Article 57	Transitional arrangements
		Sunset date ([2])
Chromium trioxide EC No: 215-607-8 CAS No: 1333-82-0	Carcinogenic (category 1A) Mutagenic (category 1B)	21 September 2017
Acids generated from chromium trioxide and their oligomers	Carcinogenic (category 1B)	21 September 2017

This Regulation shall be binding in its entirety and directly applicable in all Member States.

Done at Brussels, 17 April 2013.

For the Commission
The President
José Manuel BARROSO

Need for innovation in surface engineering

Hard chrome replacement

Properties of hard chrome:

- LOW COEFFICIENT OF FRICTION –
coefficient against steel of 0.16 (0.21 dry),

- HIGH HARDNESS
Typical values of 850 - 1050 HV

- WEAR RESISTANCE
extremely good resistance to abrasive and erosive wear

- CORROSION RESISTANCE
extremely high resistance to atmospheric oxidation, and a good resistance to most oxidising and reducing agents

- MACHINING
Can be successfully finished

Case study

Hard chrome replacement in marine engine components

WÄRTSILÄ

Wärtsilä aims to be the leader in power solutions for the global marine markets

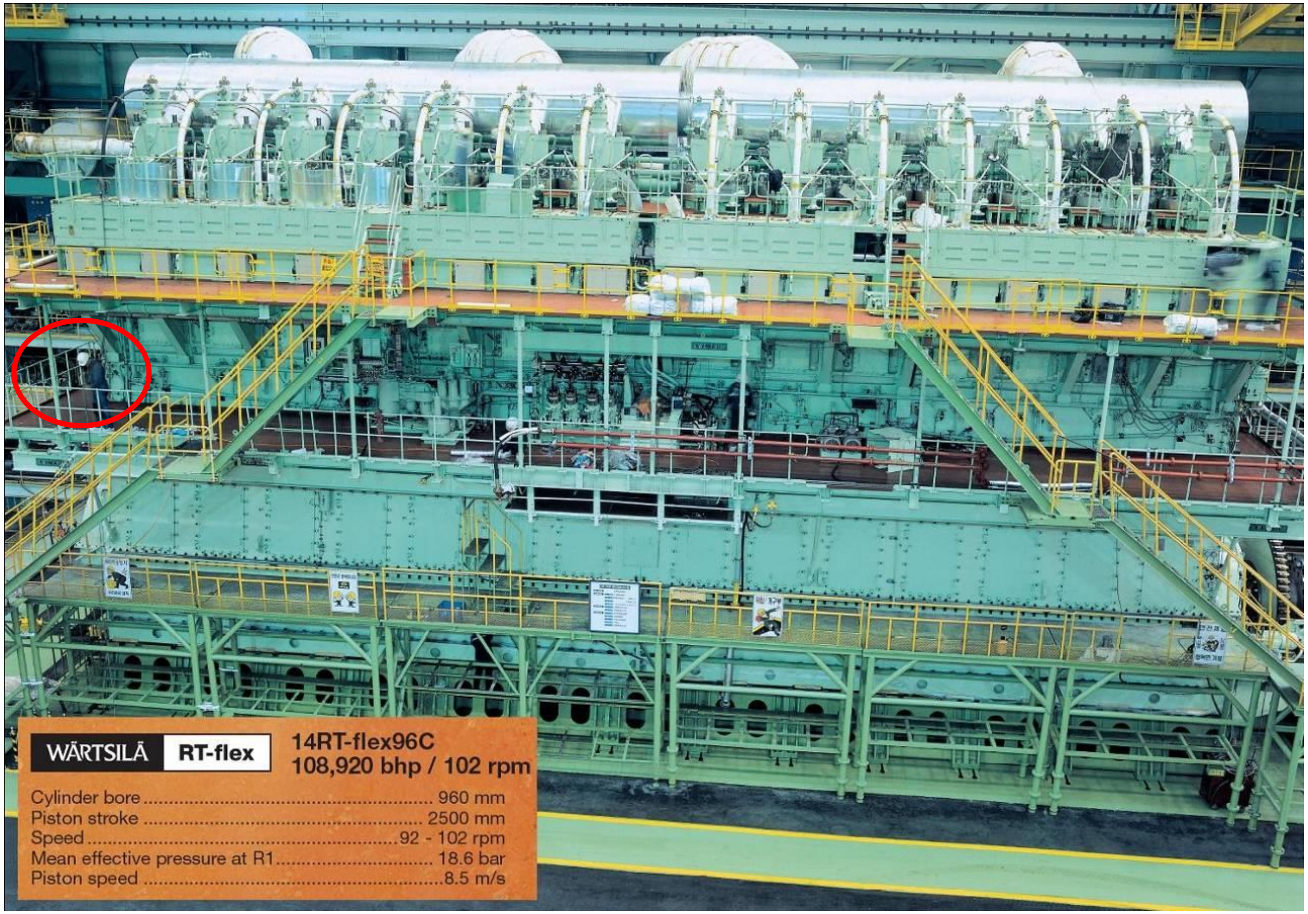
Case study

Hard chrome replacement in marine diesel engine components

WÄRTSILÄ

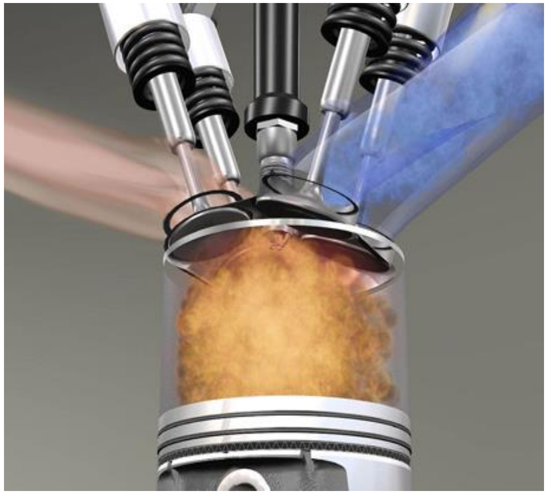
Case study

Hard chrome replacement in marine diesel engine components



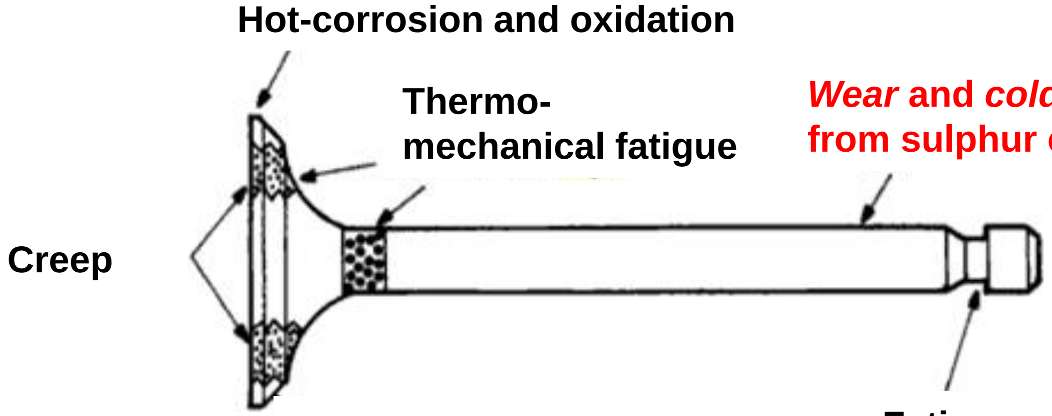
Case study

Hard chrome replacement in marine diesel engine components



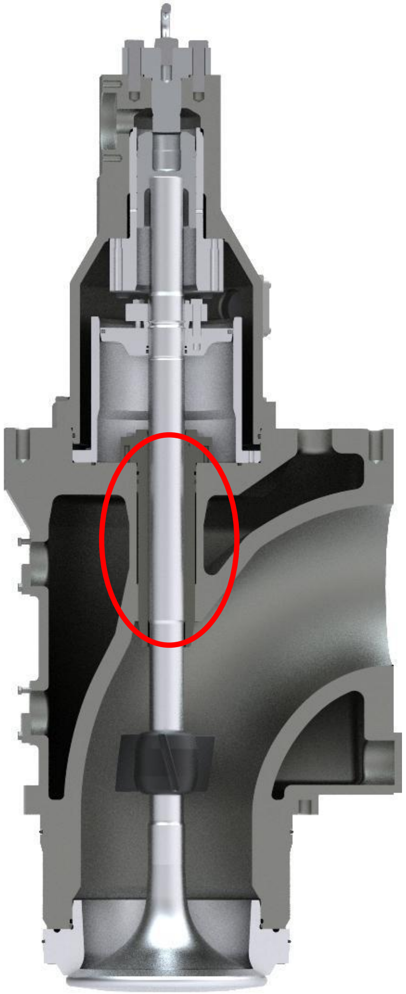
Valves problems:

- **High temperature**
- **Wear**
- **Cold and hot corrosion**

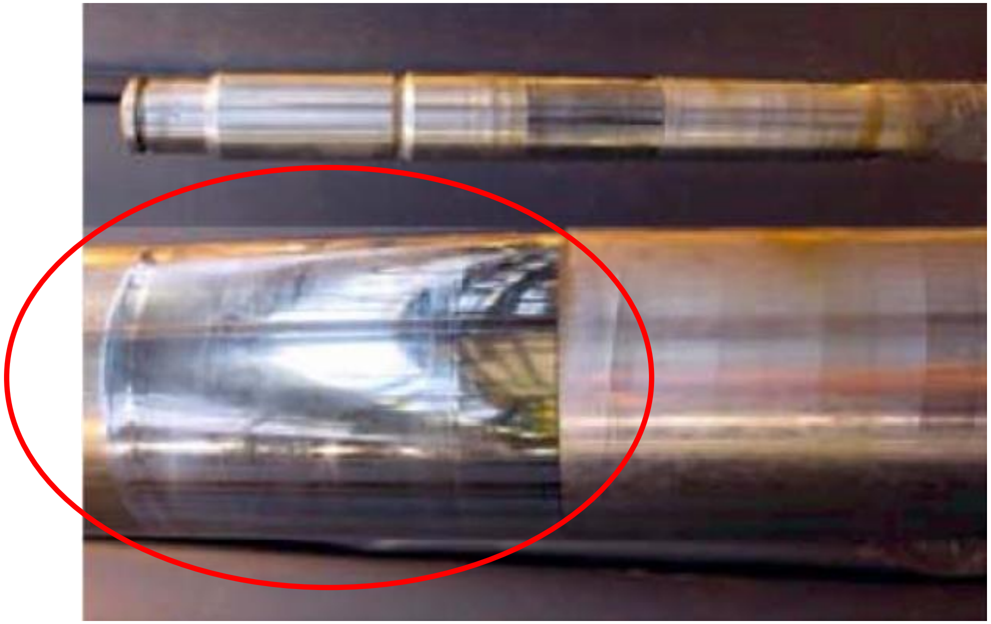


Case study

Hard chrome replacement in marine diesel engine VALVES



Problem:
Wear **and** ***cold corrosion*** **in exhaust and intake valves stem**

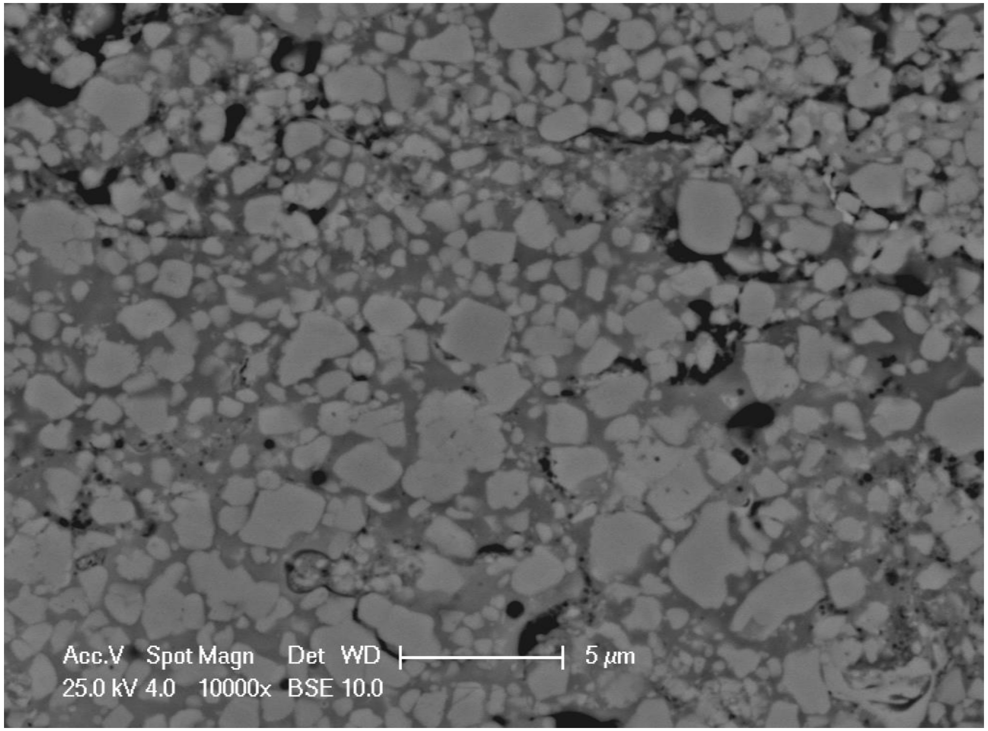


Hard chrome on stem has a short service-life

Case study

Hard chrome replacement in marine diesel engine valves

Ceramic-metal (cermet) HVOF coatings



2 phases - microstructure

Hard ceramic phase:
wear resistance

Metal matix:
toughness and corrosion resistance

Case study

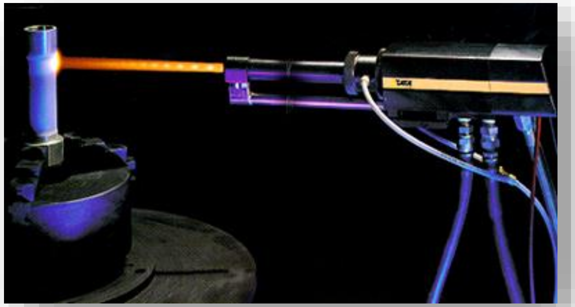
Hard chrome replacement in marine diesel engine valves

Materials (Sulzer powders):

- ✓ WC-CoCrNi — **WCN**
- ✓ (WC-Co)-NiCrSiFeBC — **WSF**
- ✓ Cr_3C_2 – 25 (Ni-Cr) — **CRC**

Facility:

HVOF – JP5000 gun



Wärtsilä requirements and constrain

Cermet HVOF coatings

- Thickness higher than150 µm
- Porosity as low as possible
- Hardness higher than 900 HV
- High deposition efficiency

Optimization of deposition parameters by *Design of Experiment (DoE)*

2 factors

1) Kerosene - O_2 flow

2) Spray distance

3 levels

1) Low

2) Medium

3) High

3^2 parameter sets

Distance (mm)	Keros. (gph) – O_2 (scfh): 5,5-1700	6-1850	6,5-2000
320			
355			
380			

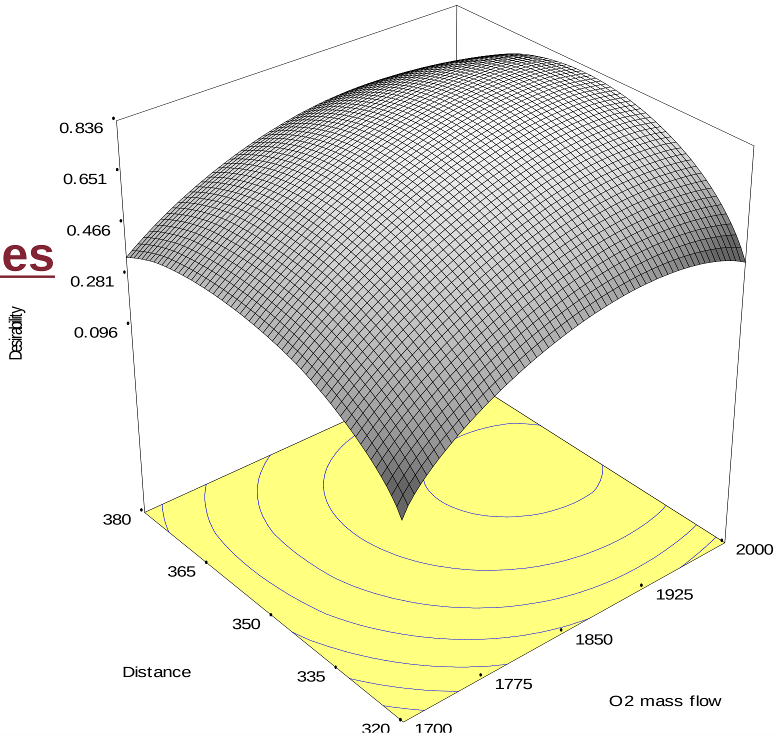
Phase 1- HVOF coatings optimization (DoE)

Investigated properties

- Deposition efficiency
- Porosity
- Hardness

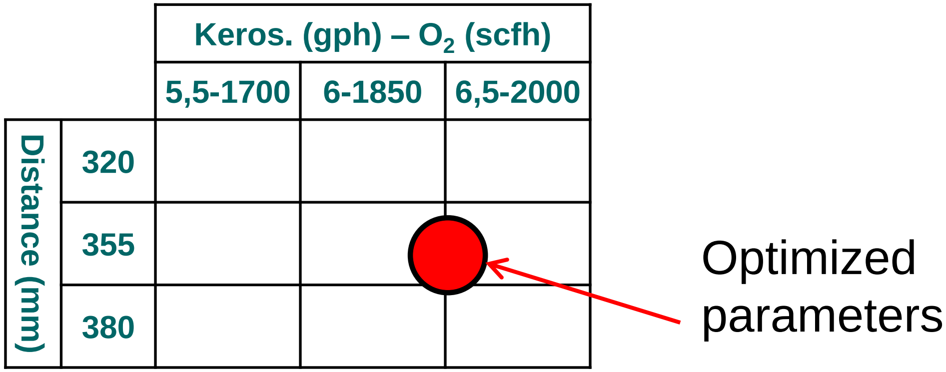
as a function of **total flow** and **spray distance**

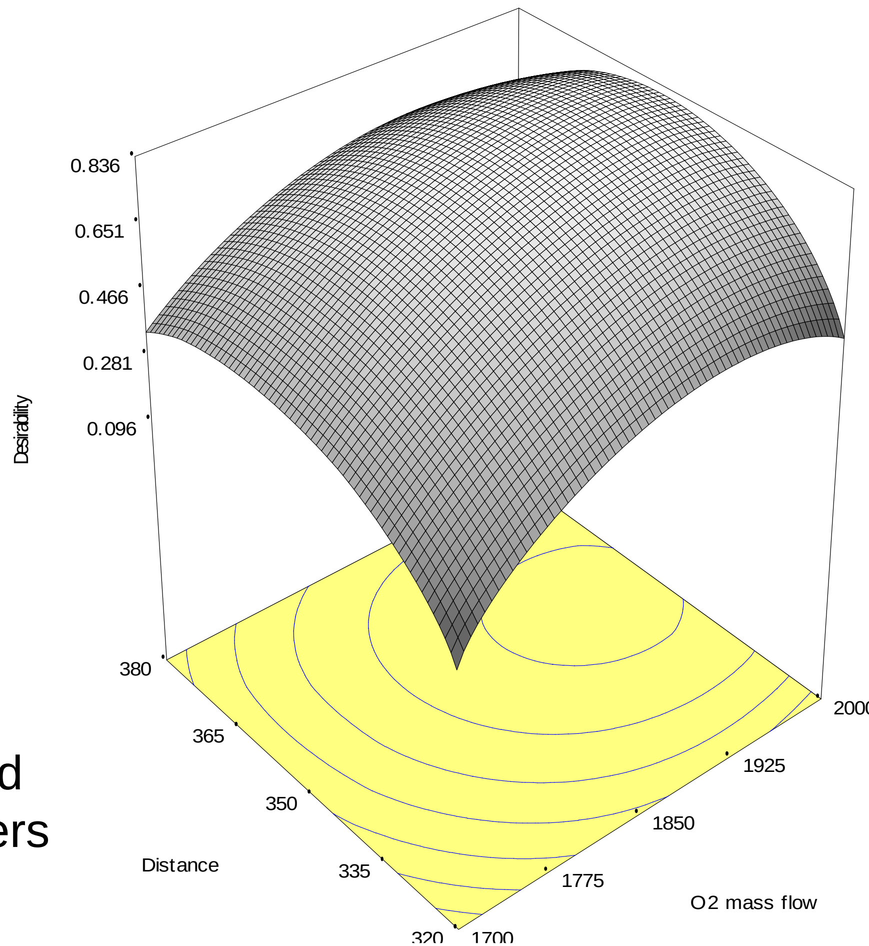
Weighted combination of these properties provide the "desirability function"



WC-CoCrNi

Properties	**Optimized value**
Deposition efficiency (um/pass)	24,3
Hardness (HV_{100})	1610
Porosity (%)	3,04
Desirability	**0,84**





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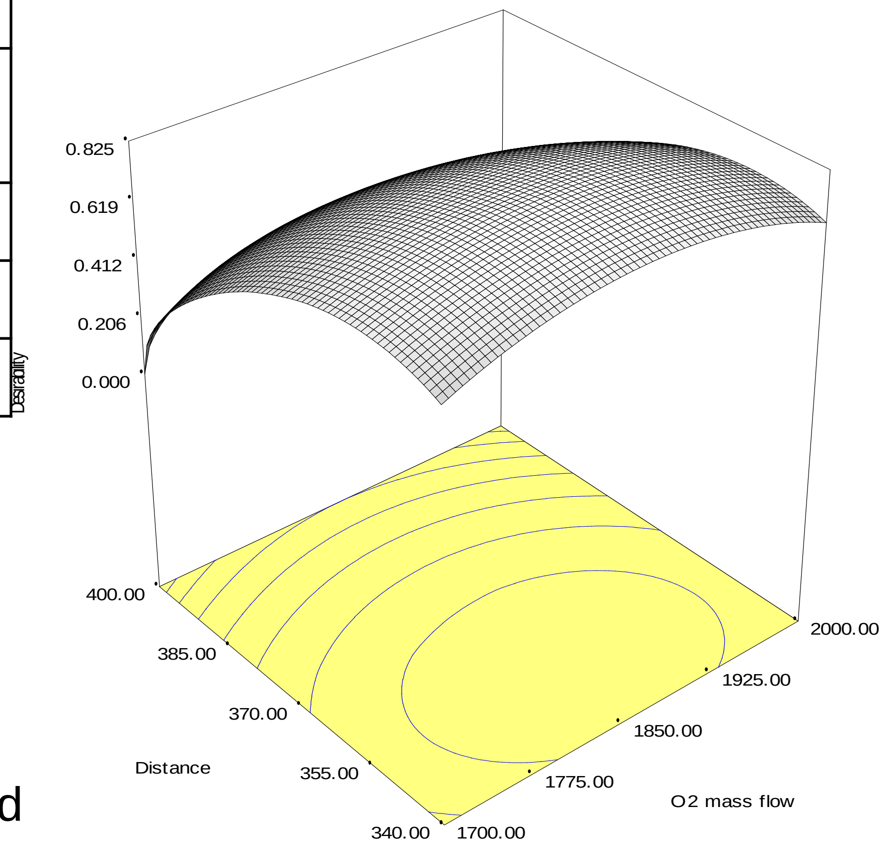
(WC-Co) - NiCrSiFeBC

Properties	**Optimized value**
Deposition efficiency (um/pass)	10,8
Hardness (HV_{50})	1053,5
Porosity (%)	1,79
Desirability	**0,82**



		Keros. (gph) – O_2 (scfh)		
		5,5-1700	**6-1850**	**6,5-2000**
Distance (mm)	**400**			
	370			
	340		●	

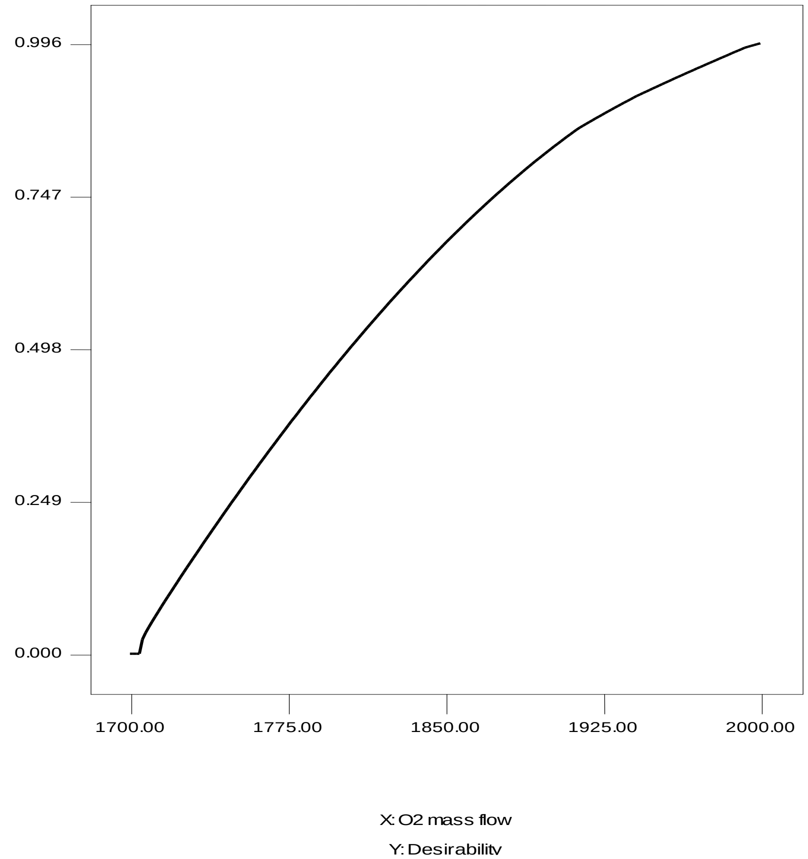
Optimized parameters

Cr_3C_2 – 25 (Ni-Cr)

Properties	Optimized value
Deposition efficiency (um/pass)	34,3
Hardness (HV_{100})	1369
Porosity (%)	4,06
Desirability	**0,996**

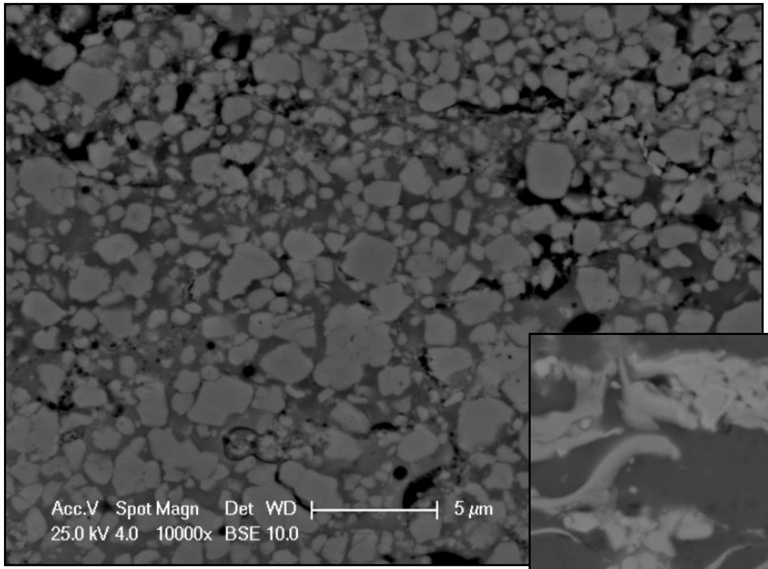
		Keros. (gph) – O_2 (scfh)		
		5,5-1700	6-1850	6,5-2000
Distance (mm)	320			
	355			
	380			

Optimized parameters

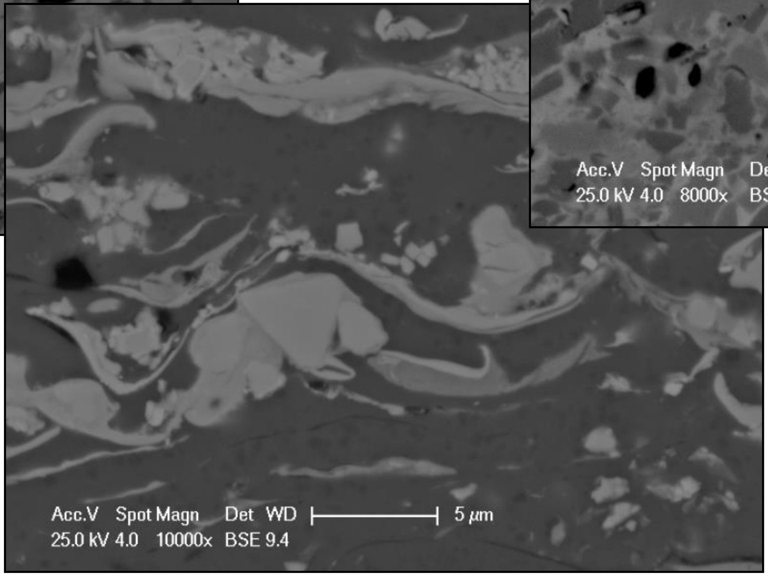


Phase 1- HVOF coatings optimization (DoE)

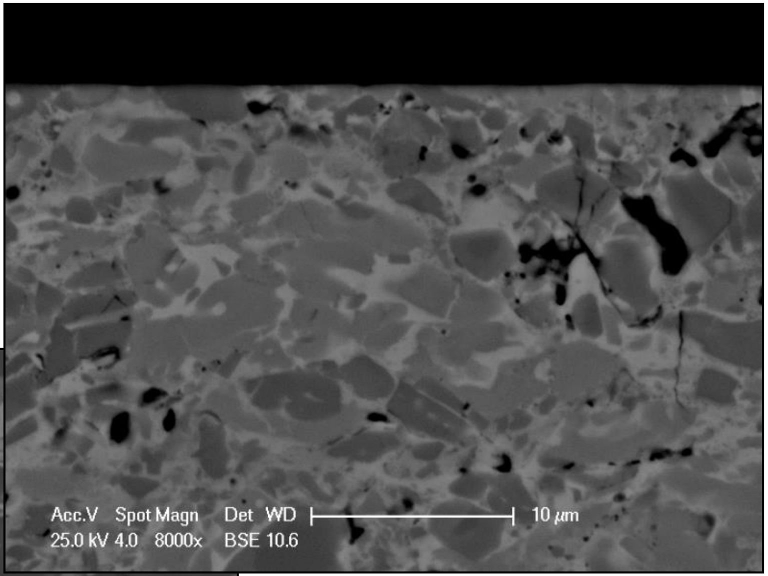
Optimized coatings



WCN



WSF



CRC

Phase 2- optimized coatings characterization

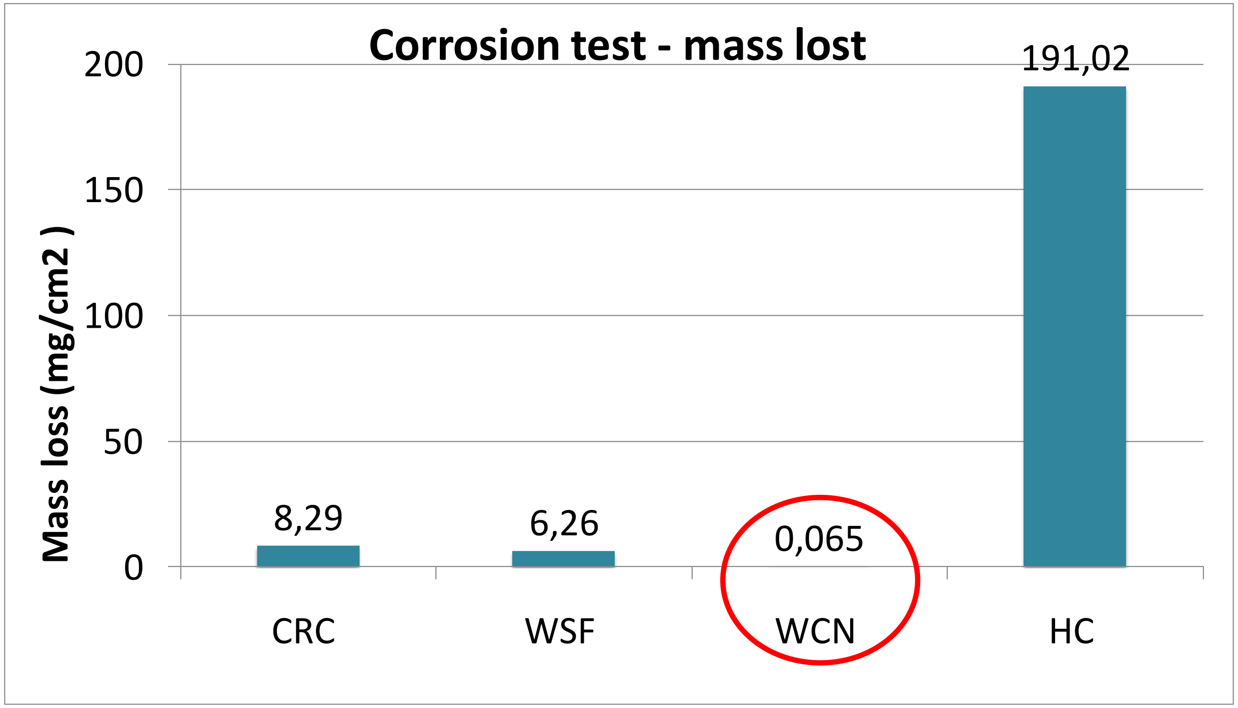
Corrosion tests

Wear tests

Phase 2- optimized coatings characterization

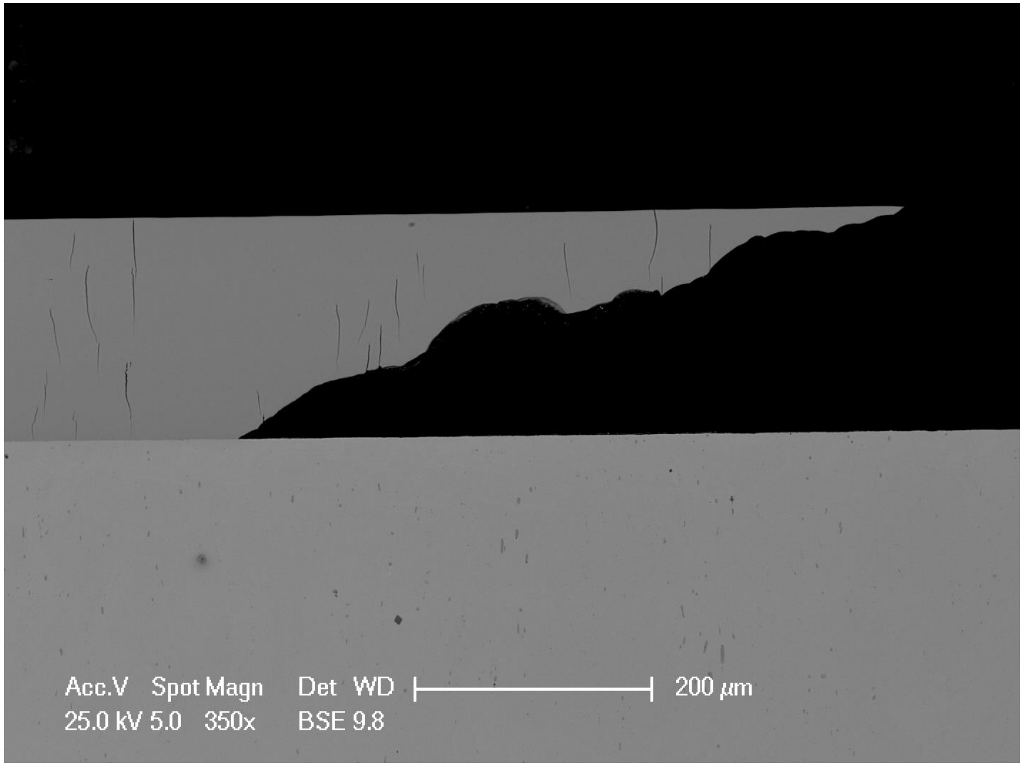
Corrosion tests

1 hour immersion test – boiling 5% H_2SO_4 solution



Phase 2- corrosion tests

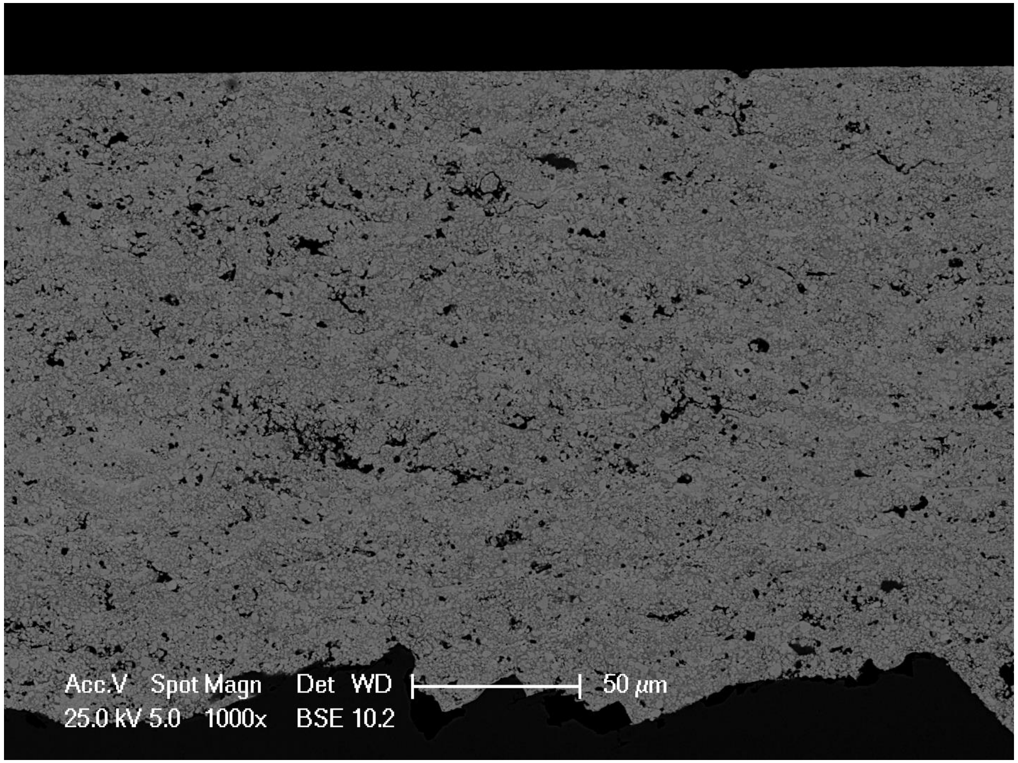
Hard chrome



Not protective

Phase 2- corrosion tests

WCN coatings

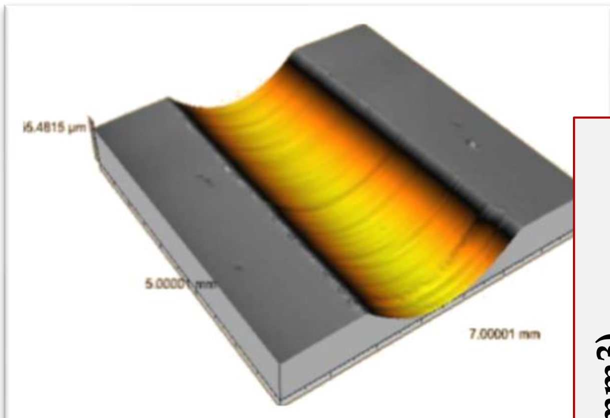


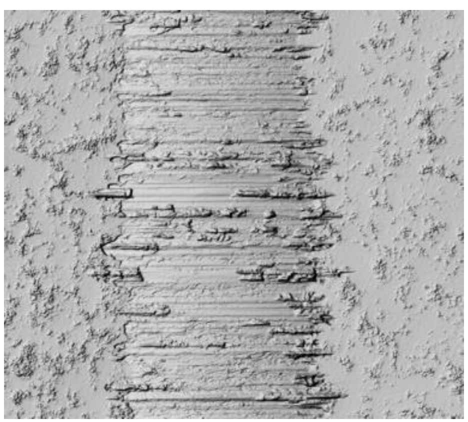
No surface damage detectable

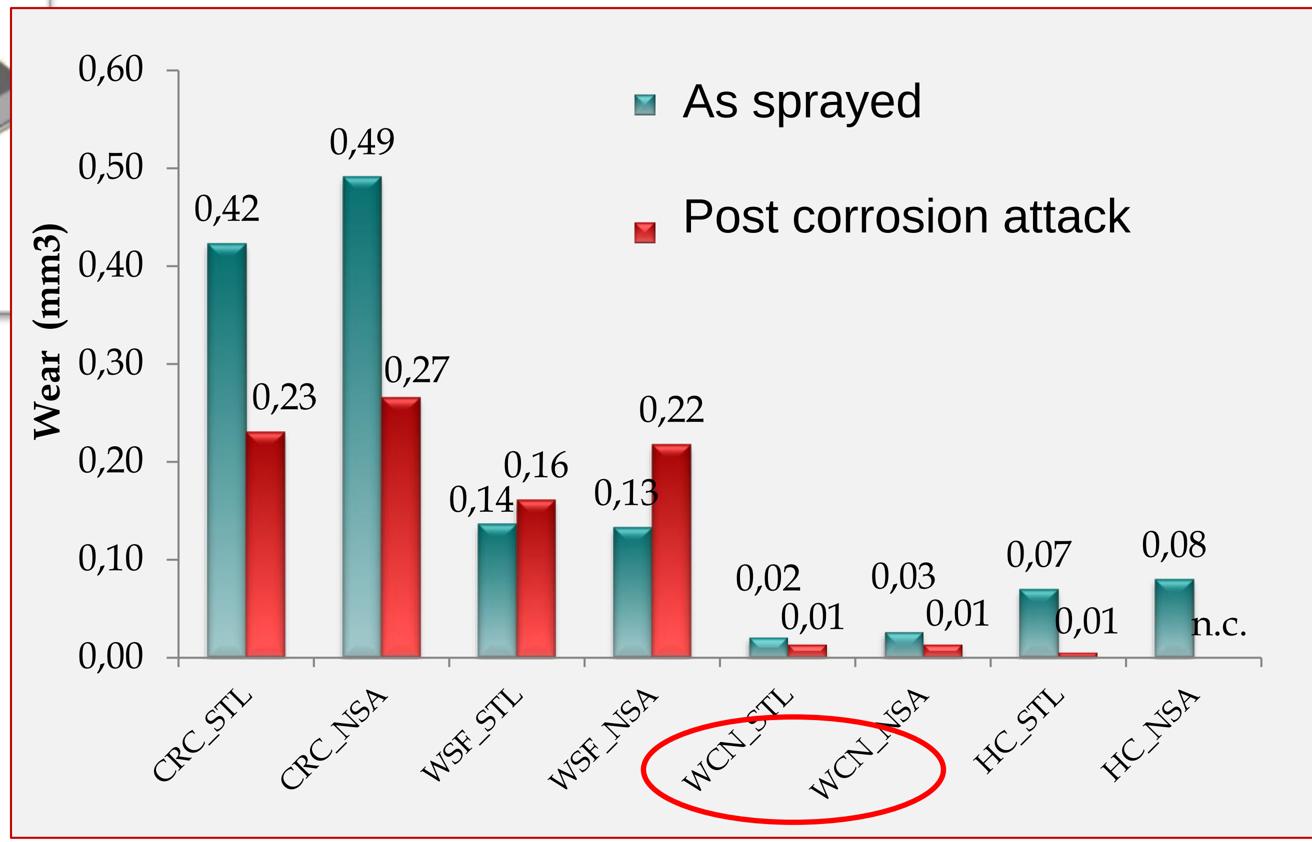
Phase 2- optimized coatings characterization

Wear tests

- Load: 91 N
- Sliding distance: 2000 m
- Speed: 1 m/s



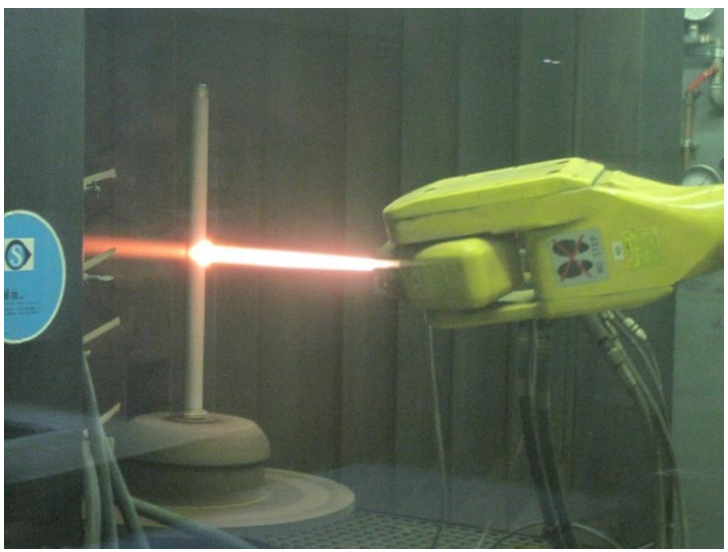




Phase 3- coating selection for valve deposition

WC-CoCrNi:

- Highest hardness
- Lowest wear rate
- Lowest corrosion rate
- Good density
- High deposition efficiency

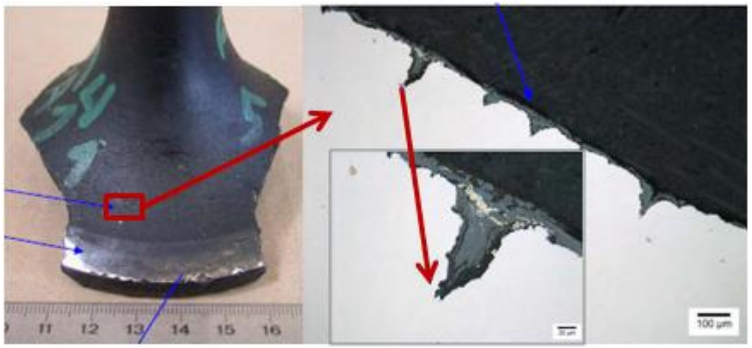


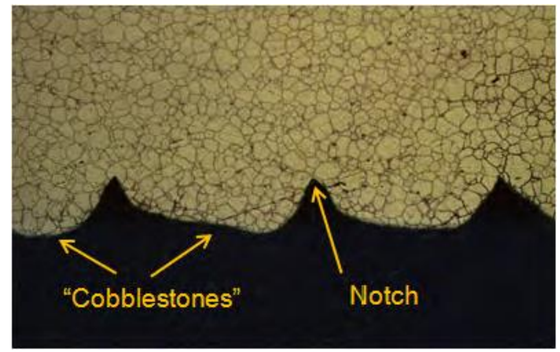
- WC-CoCrNi coating was selected

- Coated valves tested for 3 years on a Wartsila test engine

Innovative coatings for hot corrosion

Case study: Hot corrosion on marine diesel engines valves





$$Na_2O \cdot 6V_2O_5 \leftrightarrow Na_2O \cdot V_2O_4 \cdot 5V_2O_5 + \frac{1}{2}O_2$$

$$5Na_2O \cdot 12V_2O_5 \leftrightarrow 5Na_2O \cdot V_2O_4 \cdot 11V_2O_5 + \frac{1}{2}O_2$$

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Aggressive environment produced by high impurity contents within the fuel: V, Na, S.

Innovative coatings for hot corrosion

Multiphase cermet coatings: CrystalCoat

(19) **United States**

(12) **Patent Application Publication**

VERLOTSKI

(10) **Pub. No.: US 2008/0317966 A1**

(43) **Pub. Date: Dec. 25, 2008**

(54) **THERMALLY SPRAYED GASTIGHT PROTECTIVE LAYER FOR METAL SUBSTRATES**

(75) Inventor: **Vadim VERLOTSKI**, Wuppertal (DE)

Correspondence Address:
KATTEN MUCHIN ROSENMAN LLP
575 MADISON AVENUE
NEW YORK, NY 10022-2585 (US)

(73) Assignee: **MARKISCHES WERK GMBH**, Halver (DE)

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H01L 21/316 (2006.01)

(52) **U.S. Cl.** **427/452**; 427/576; 428/220; 106/287.18

(57) **ABSTRACT**

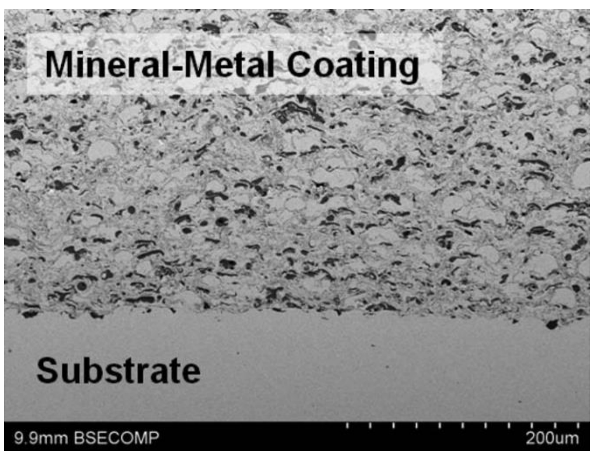
In a thermally sprayed, gastight protective layer for metal substrates, especially those based on Fe, Ni, Al, Mg and/or Ti, wherein the spray powder for the purpose comprises at least

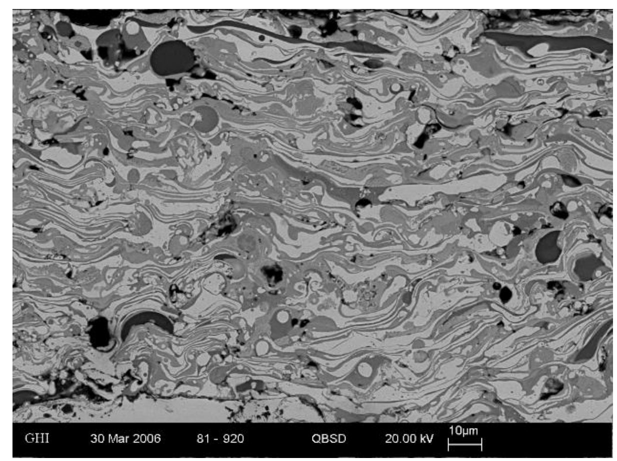
Innovative coatings for hot corrosion

Multiphase cermet coatings: CrystalCoat

Metal alloy | SiO_2 | Basalt | Oxide | Other silicates

CRYSTALCOAT





Innovative coatings for hot corrosion

Case study: Hot corrosion on marine diesel engines valves

Aim: development of innovative thermal spray coatings alternative to Crystal Coat

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Commercial (non standard) tested solutions

- ✓ Cr_3C_2 – NiCr
- ✓ Cr_3C_2 – NiCrAlY
- ✓ Cr_3C_2 – CoNiCrAlY
- ✓ Cr_3C_2 – self fusing alloy

Development of innovative solutions

- ✓ Mullite – nano SiO_2 – NiCr

Innovative coatings for hot corrosion

Phase 1- coatings optimization (DoE)

- Thickness higher than150 µm
- Porosity as low as possible
- High deposition efficiency

→ Optimization of deposition parameters by *Design of Experiment (DoE)*

2 factors

1) Kerosene - O_2 flow
2) Spray distance

3 levels

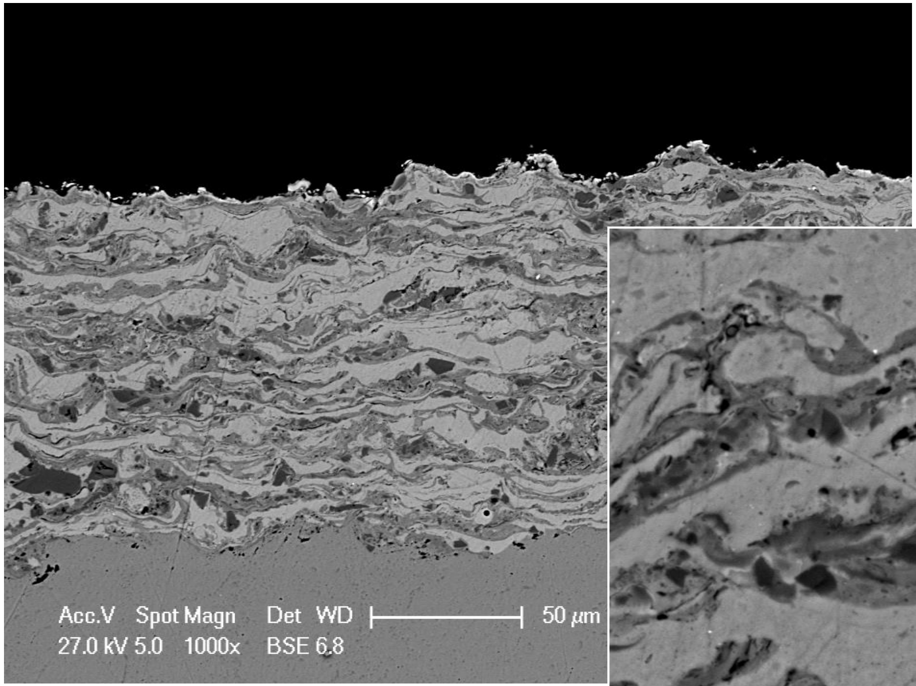
1) Low
2) Medium
3) High

3^2 parameter sets

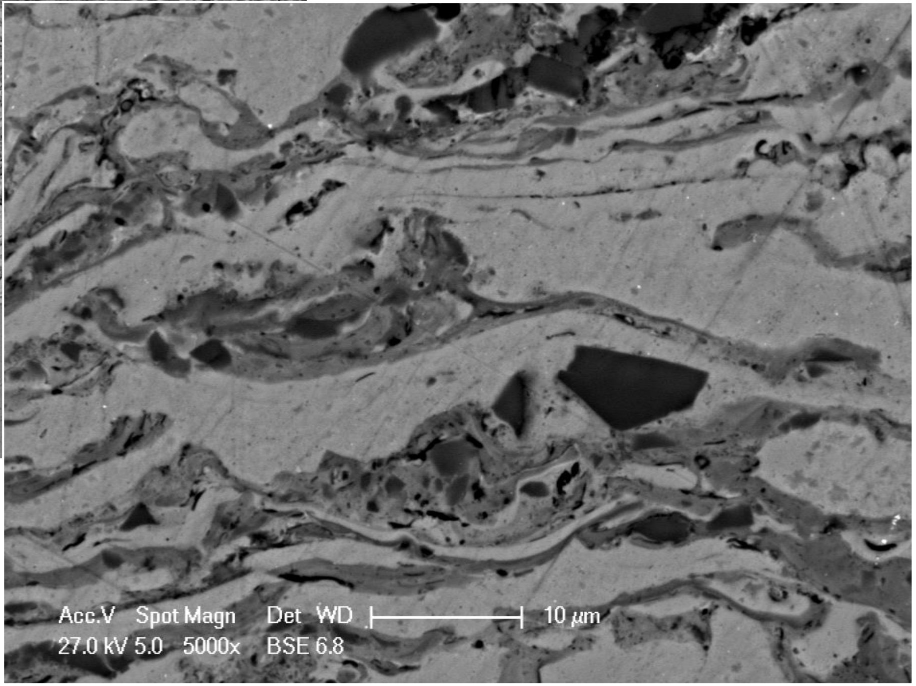
		Keros. (gph) – O_2 (scfh)		
		5,5-1700	6-1850	6,5-2000
Distance (mm)	320			
	355			
	380			

Example: optimization of Cr_3C_2 - self fusing alloy

Optimized coating



Very low porosity (< 1 %)

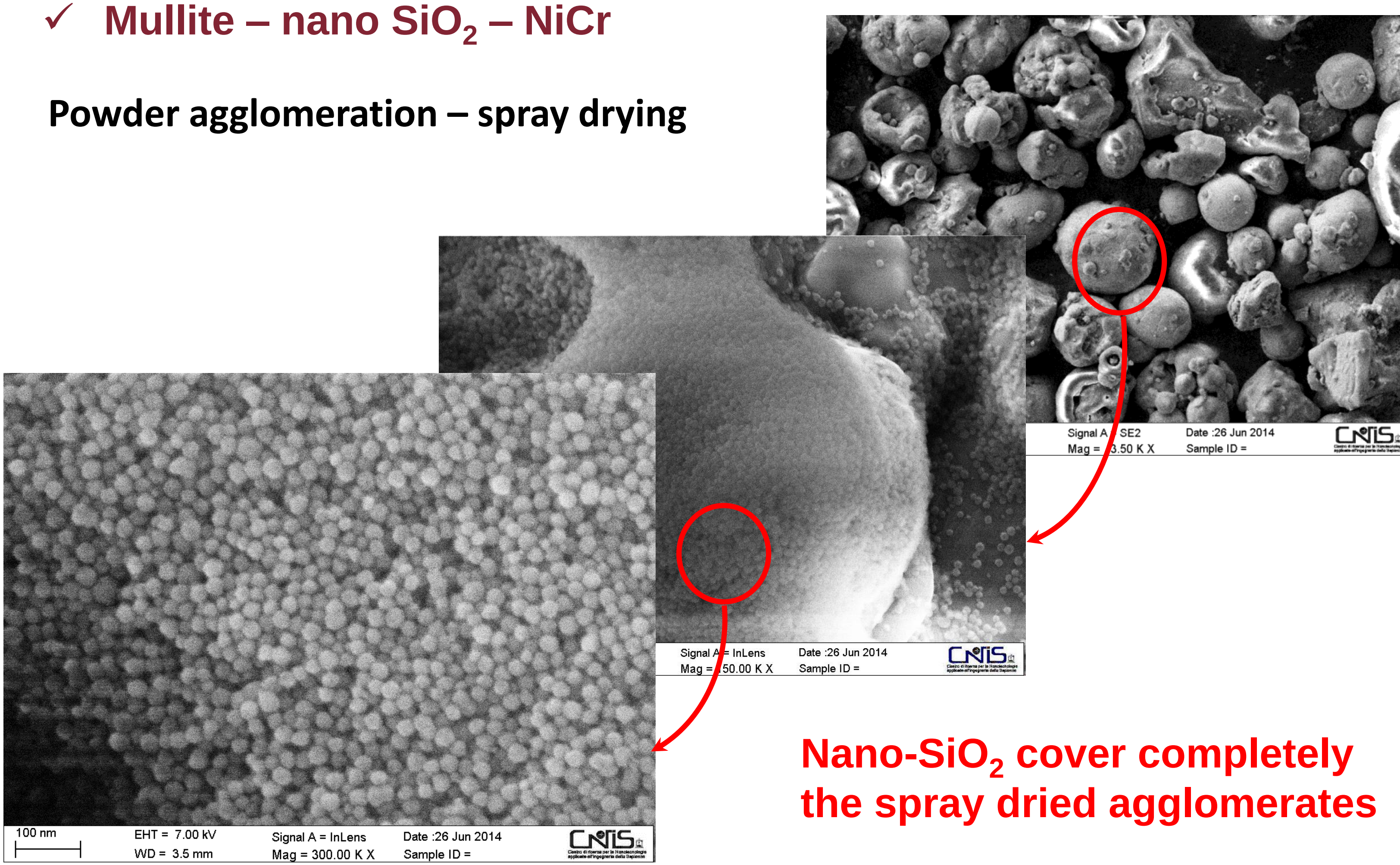


Ceramic phase dispersed in multiphase metallic matrix

Innovative coatings for hot corrosion

✓ **Mullite – nano SiO_2 – NiCr**

Powder agglomeration – spray drying

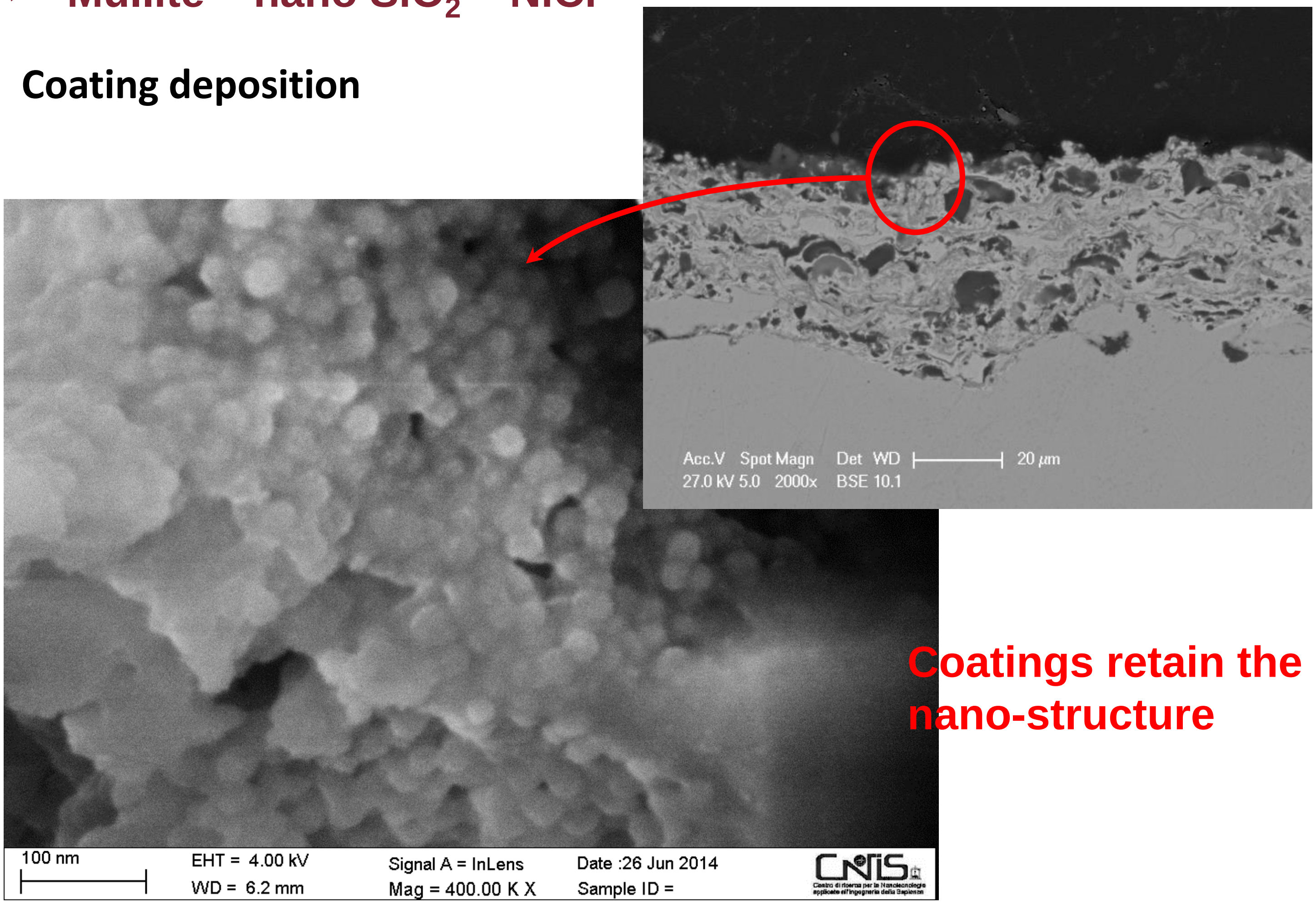


Nano-SiO_2 cover completely the spray dried agglomerates

Innovative coatings for hot corrosion

- ✓ **Mullite – nano SiO_2 – NiCr**

Coating deposition



Coatings retain the nano-structure

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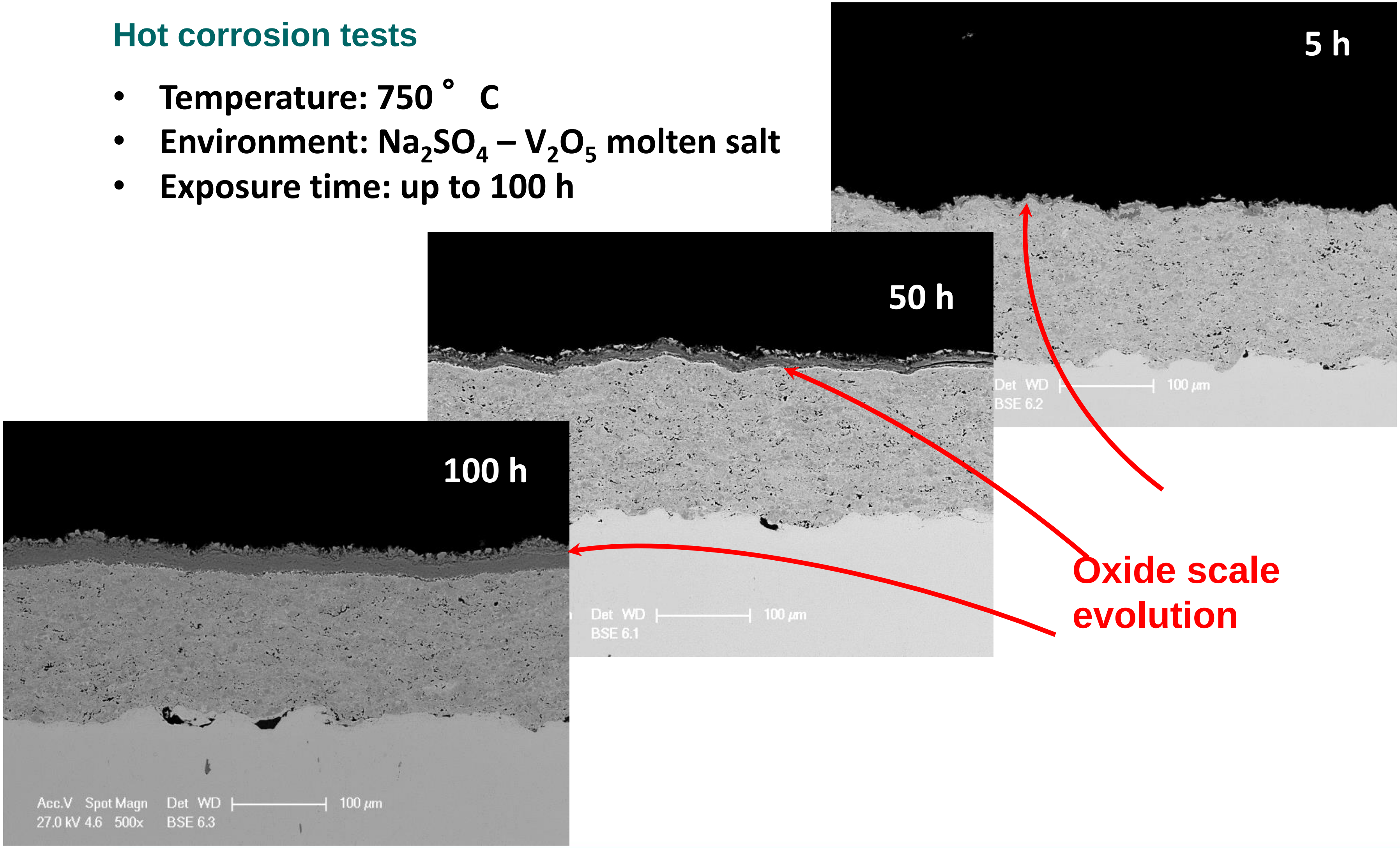
Innovative coatings for hot corrosion

Hot corrosion tests

- **Temperature: 750 ° C**
- **Environment: Na_2SO_4 – V_2O_5 molten salt**
- **Exposure time: up to 100 h**



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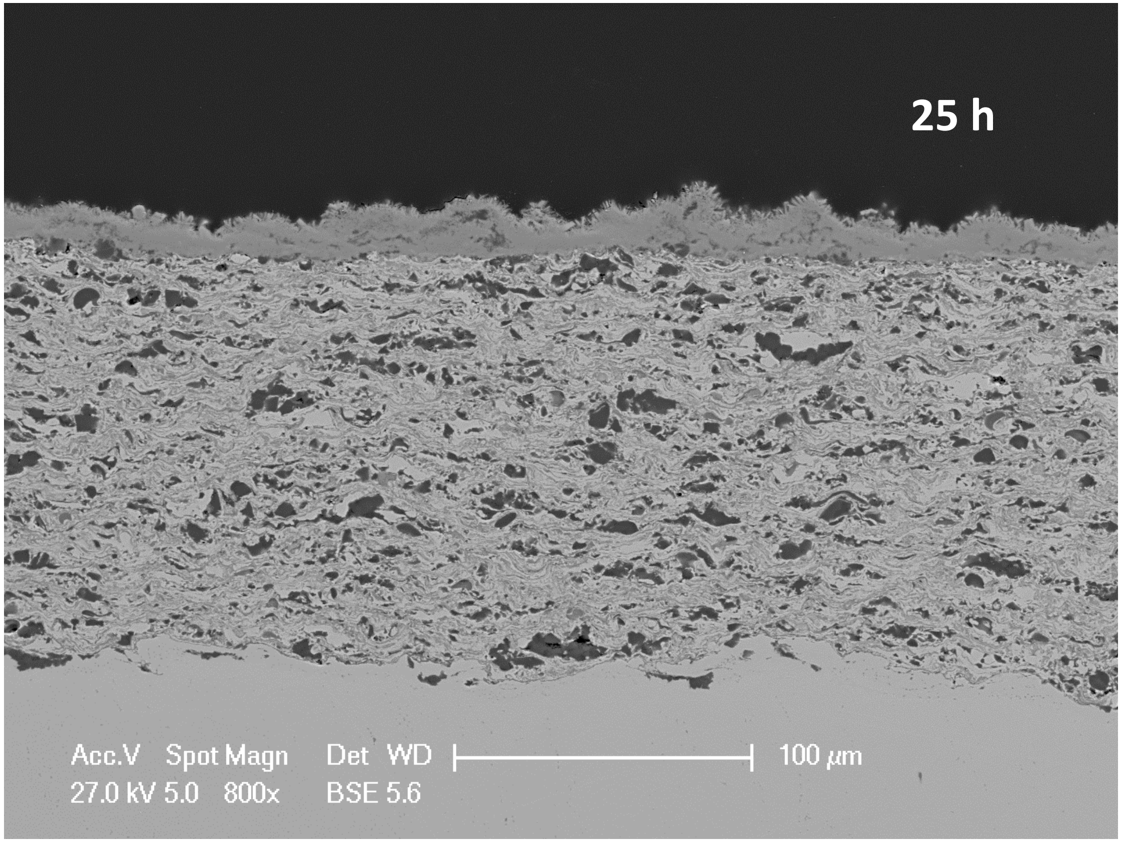
Hot corrosion tests

Nanostructured coating



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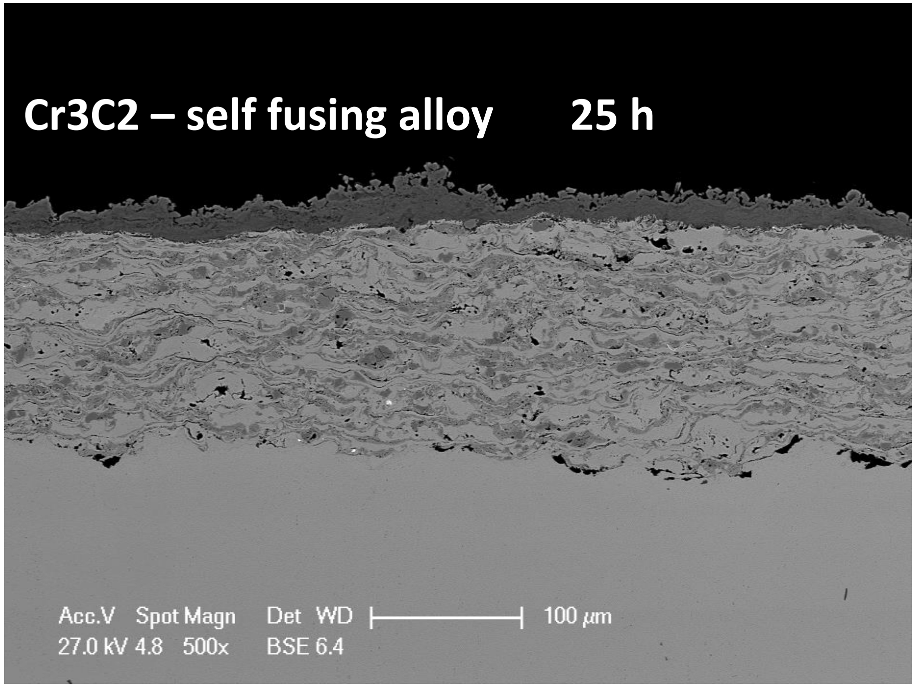
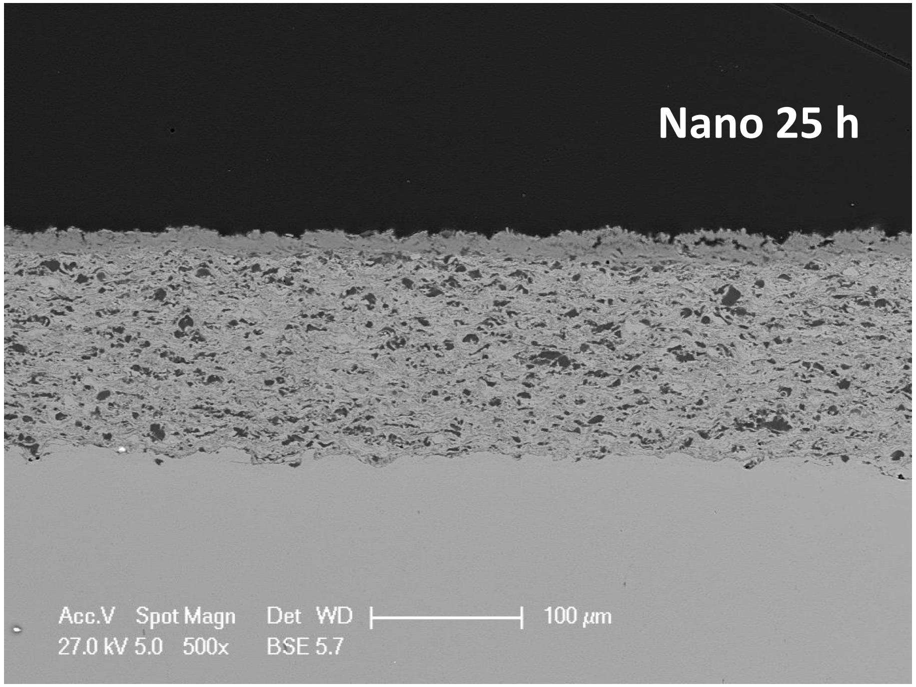
Hot corrosion tests

Comparison between nanostructured and self fusing coatings





Thinner oxide scale in nano-coating

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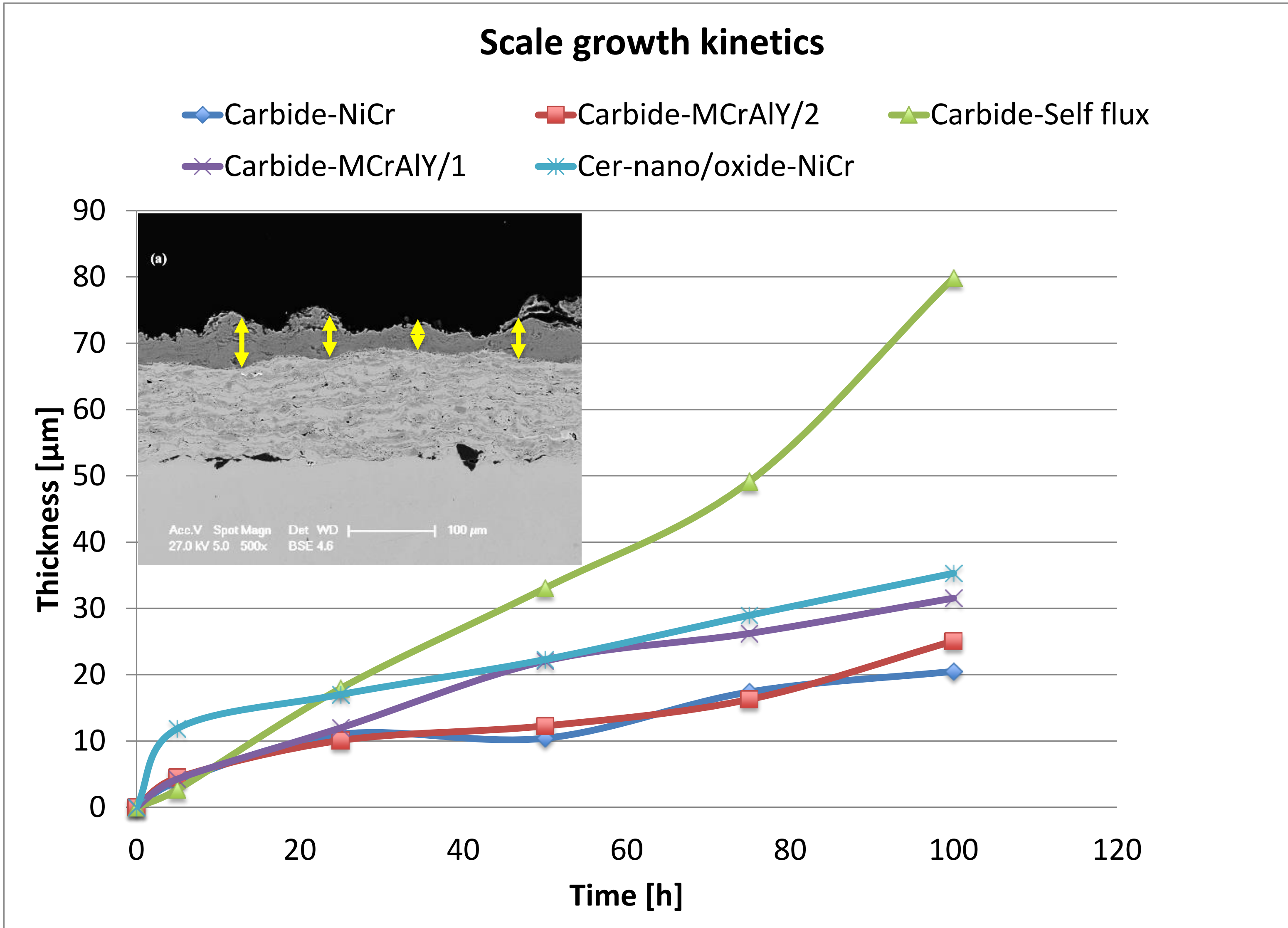
Corrosion kinetics



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