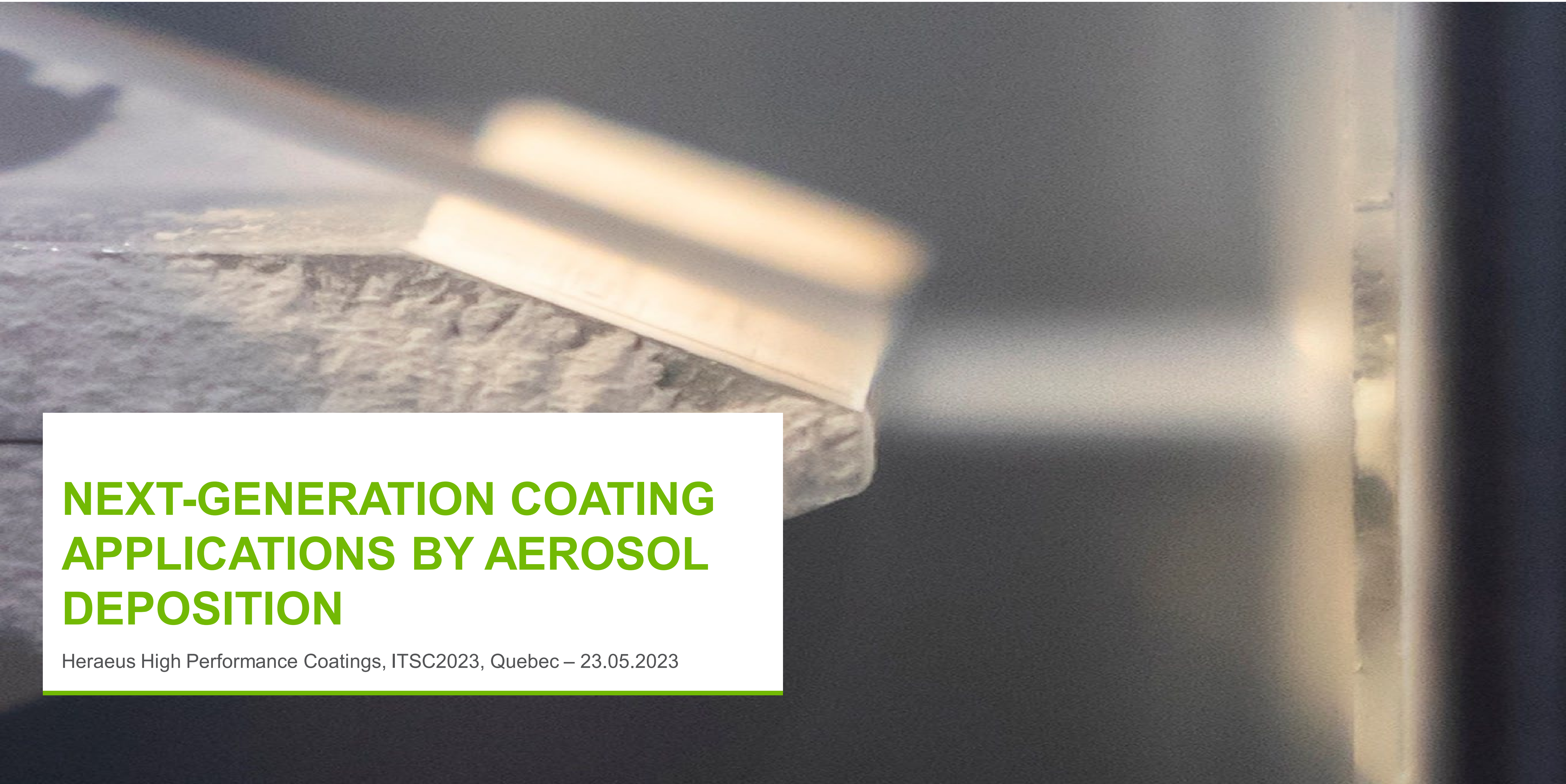

NEXT-GENERATION COATING APPLICATIONS BY AEROSOL DEPOSITION

Heraeus High Performance Coatings, ITSC2023, Quebec – 23.05.2023

Heraeus

OUTLINE

1) Aerosol Deposition by Heraeus High Performance Coatings

2) Next Generation Coatings for semicon and medical applications:
   YAG & Si3N4

3) Significant Service Life Extension for High-Temperature Nickel Alloys

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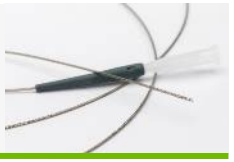
THE HERAEUS BUSINESSES – BROADLY DIVERSIFIED

Heraeus Holding

Global Business Units

Heraeus **Comvance**


Heraeus **Conamic**


Heraeus **Medevio**


Heraeus **Electronics**


Heraeus **Epurio**


Heraeus **Medical**


Heraeus **Photovoltaics**


Heraeus **Noblelight**

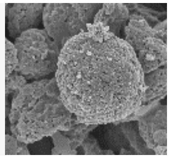

Norwood Medical


Heraeus **Electro-Nite**


Heraeus **Precious Metals**


Start-ups

Heraeus **Amloy**


Heraeus **Battery Technology**


Heraeus **Printed Electronics**


Heraeus **Remloy**


Heraeus **High Performance Coatings**


Investments

revalyu


Forciot


Mo-Sci


ETS Technologies


…

HPC'S CORE TECHNOLOGY: AEROSOL DEPOSITION

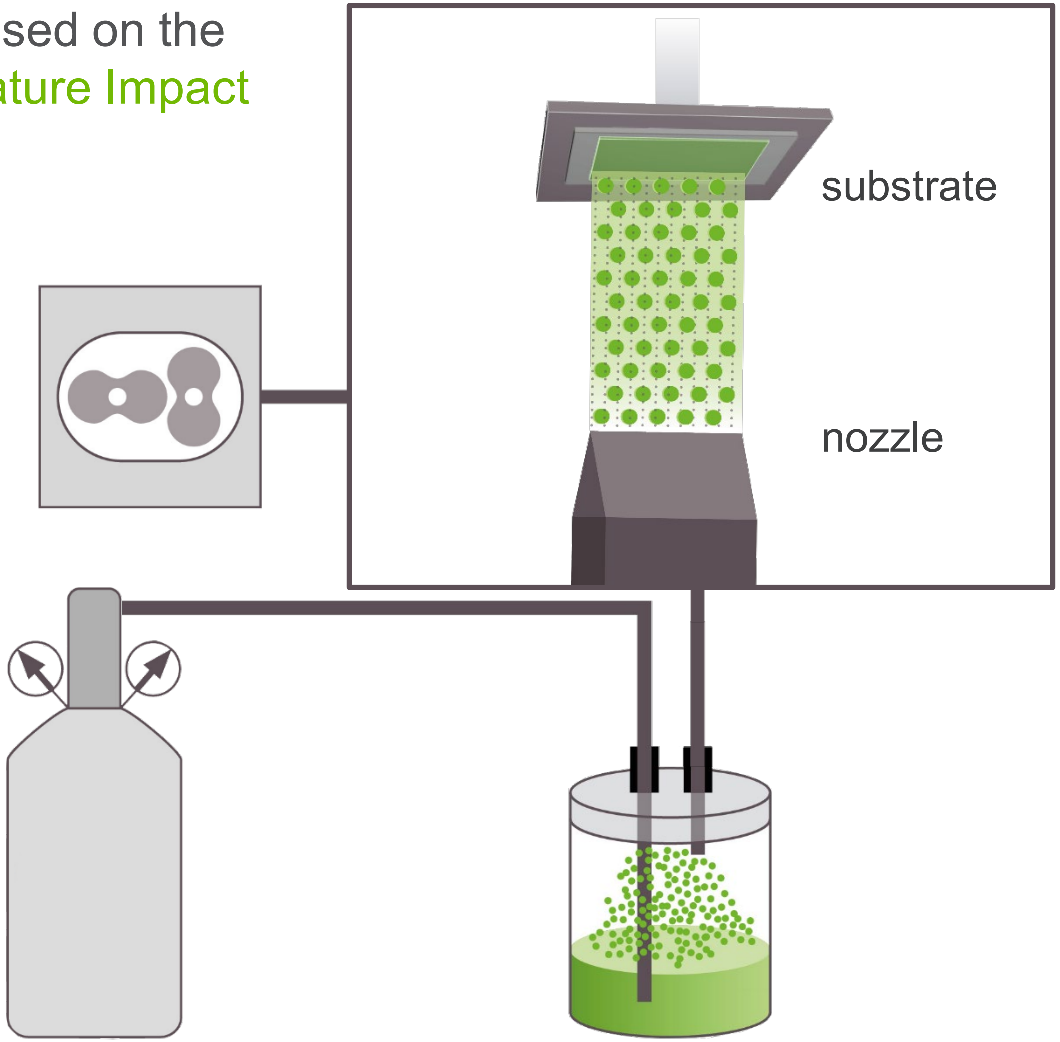
The AD is a coating method based on the mechanisms of Room Temperature Impact Consolidation

vacuum pump

low vacuum (1 mbar)

carrier gas

e.g. compressed air



deposition chamber

particles accelerated to several 100 m/s sprayed on substrate fracture due to high kinetic energy and form a compact layer

high process stability and reproducibility due to generic nozzle design

aerosol generator

Particles of coating material (sub-µm to several µm)

Heraeus

UNPRECEDENTED MATERIAL FREEDOM

Aerosol Deposition – a unique coating method

Room Temperature Coating

- Ceramics
- Metals
- Unprecedented material combinations and mixtures

Coating Quality

- Very good adhesion
- Minimum surface roughness increase
- Very high compactness
- 1 – 100 µm

Cost Effective

- High deposition rates
- Moderate equipment costs
- Low energy consumption

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COMPARISON OF DIFFERENT COATING TECHNOLOGIES

	Aerosol Deposition	CVD/PVD	Thermal Spray	Cold Spray
Material Choice	Metals, Ceramics, Composites	Metals, Ceramics, Composites	Metals, Ceramics, Composites	Metals, Cermets
Deposition Rate	High	Low	High	Very High
Temperature	Low (RT)	Medium/High	High	Medium (~ 300 °C)
Vacuum	Low Vacuum	UHV	Atmospheric	Atmospheric
Scale-Up	Medium Parts	Difficult	Large Parts	Large Parts
Thickness	1 – 100 µm	~ 1 µm	> 50 µm	> 50 µm
Adhesion	Very Good	Poor	Good	Good
Conformity	Good	Very Good	Poor	Poor
Costs	Low	High	Medium/Low	Medium

TESTED COATING AND SUBSTRATE MATERIALS

HPC has an unprecedented portfolio of coating materials and material mixtures for all types of substrates

11 ceramic and 4 metal coatings are available off the shelf
- mixtures of materials possible

Ceramic Coatings

- α-Aluminum Oxide
- γ-Aluminum Oxide
- Yttrium Oxide
- ZTA (Zirconia toughened Alumina)
- Aluminum Nitride
- Spinel (Magnesium Aluminate)
- MSZ (Magnesia stabilized Zirconia)
- UV luminescent compounds
- Silicon Nitride
- YSZ (Yttria-stabilized Zirconia)
- YAG (Yttrium Aluminum Garnet)

Metal Coatings

- Silver (Ag)
- Copper (Cu)
- Tin (Sn)
- Tungsten (W)

Coating Mixtures

- Aluminum Oxide / Pore-forming agent
- AlN / TiN

New coatings and substrates are continuously tested

Selection of tested substrates

- Metals e.g., steel, aluminum, copper
- Ceramics e.g., Al_2O_3 , YSZ, AlN , Si_3N_4
- Glass
- Silicon
- Polymers
- Structured substrates e.g., gold or platinum electrodes on ceramics

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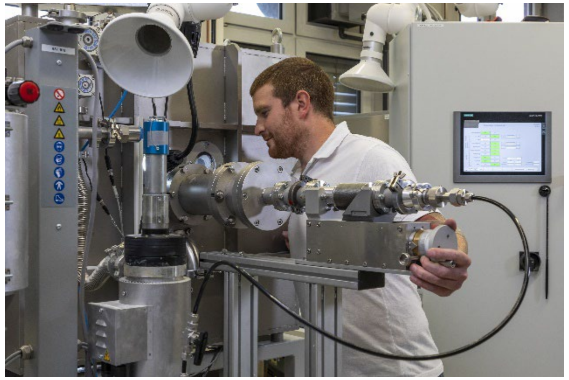
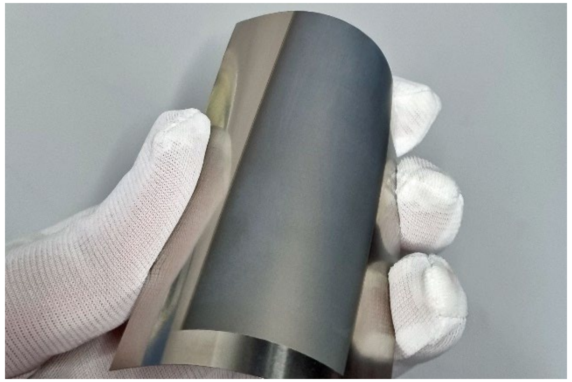
OUR SERVICES

We accompany customers from initial feasibility study to introducing this new process into series production.



Evaluation

- Material screening
- Feasibility studies
- Process customization



Prototype & (Small) Series

- Prototype manufacturing
- (Small) series production

Equipment Supply

- Custom made production equipment
- Standardized R&D equipment

Material Supply

- Reliable material supply
- Guaranteed result if material & equipment is from Heraeus

APPLICATIONS

E-Mobility

e.g. electrically insulating coatings (laminated permanent magnets, ball bearings)

Industrial Equipment

e.g. anti-corrosion coatings for high temperature alloys (furnaces), separator layers in high temperature processes

Sensors

e.g. protective coatings for high-temperature sensors

Medical Area

e.g. development of antiseptic coatings

Electronics

e.g. electrically insulating coatings, functional coatings (MLCC, storage devices, piezoelectric sensors)

Semiconductor Production

e.g. etch resistant coatings for plasma etch chambers

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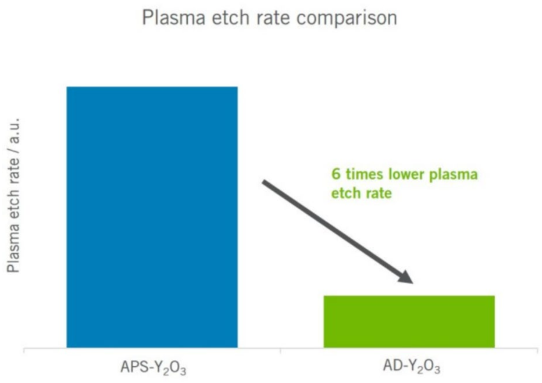
Heraeus

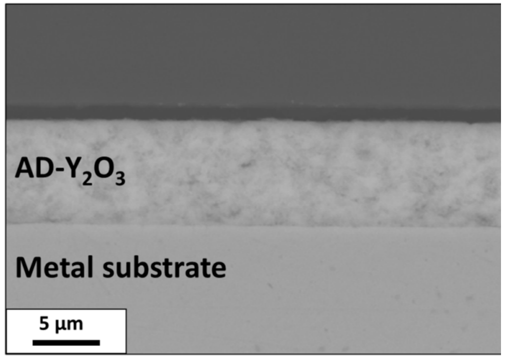
ETCH RESISTANT COATINGS FOR PLASMA ETCH CHAMBER PARTS

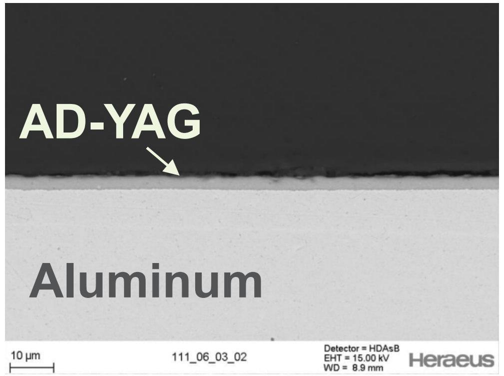
Y_2O_3 and YAG coatings by Aerosol Deposition

Next generation Plasma resistant coatings: AD-YAG

- **Progress in EUV** lithography allows further miniaturization, creating challenges for established coating materials and coating methods in the plasma etch chamber
- < 17 nm particles become big issue for current nodes → AD-Y_2O_3 not good enough anymore → **Next generation AD-YAG coatings**
- YAG can be done very well by AD not so easy by other deposition methods







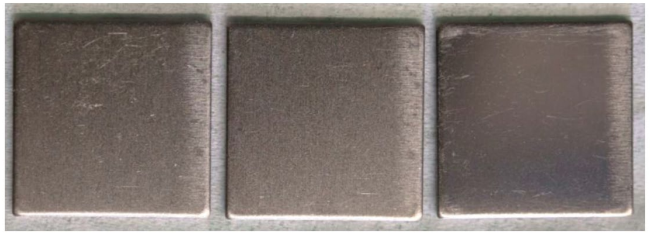
SI3N4 COATINGS BY AEROSOL DEPOSITION

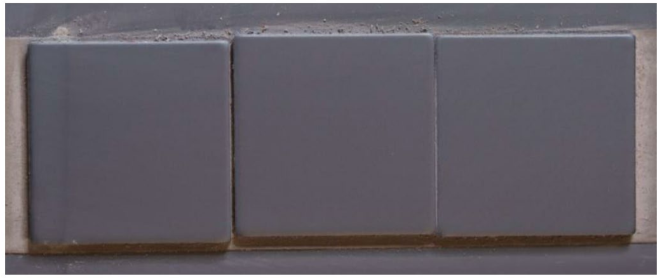
- Thermal Spraying of Si_3N_4 highly challenging: dissociation above 1800°C, oxidization
- Limited success with inflight nitridation or reactive spray processing
- State of the art Si_3N_4 coatings by CVD → costly process

Si_3N_4 coatings applied by Aerosol Deposition

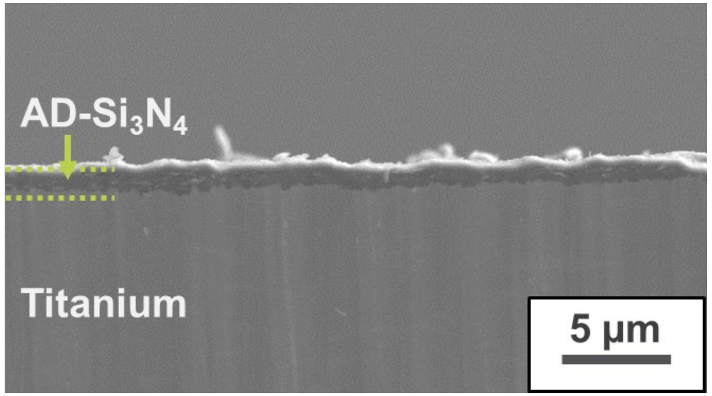
- Coating of Si_3N_4 directly on the part at room temperature
- Stoichiometric Si_3N_4 films with no impurities or unwanted embrittling phases
- Large variety of processable substrates (metals, ceramics, polymers)
- Very good mechanical properties of AD-Si_3N_4 films e.g.:

  R_a = 0,3 µm, R_z = 1,5 µm (unetched)
  Thermo-shock: > 1000 cycles: -65 °C ↔ 150 °C
  Adhesion > 30 MPa, no change in appearance





Titanium plates uncoated (top) and AD-Si_3N_4 coated (bottom)



SEM cross-section AD-Si_3N_4 on Ti

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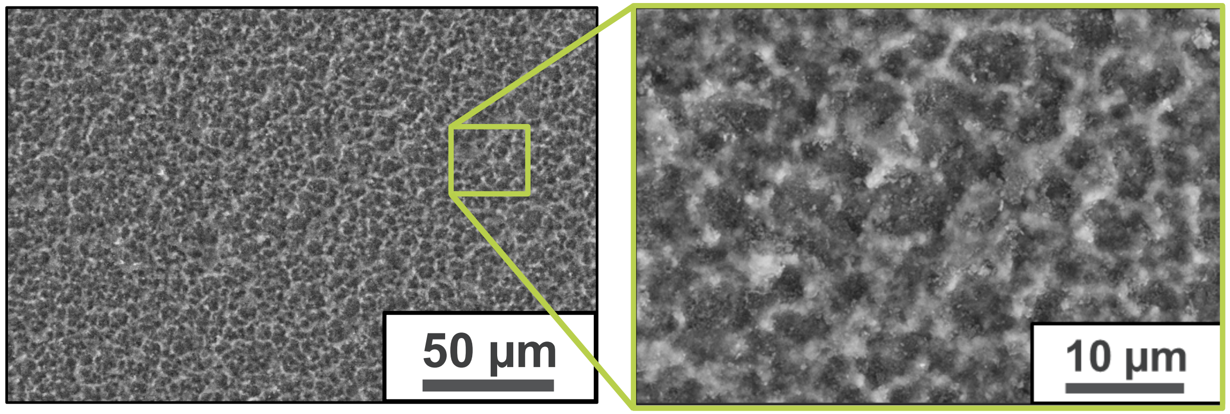
EXEMPLARY SI3N4 COATINGS

Si_3N_4 as antibacterial and antiviral coating

- β-Si_3N_4 coatings exhibit anti-viral and antibacterial characteristics
- **Coating of AD-Si_3N_4 on complex geometries replacing costly CVD coating processes**
- Crater like surface structure in as-deposited state
  → large surface with high contact angle (hydrophobic)



SEM top views of AD-Si_3N_4 film

Examples of AD-Si_3N_4 coated products: dental implant (top) and bone screw (bottom)

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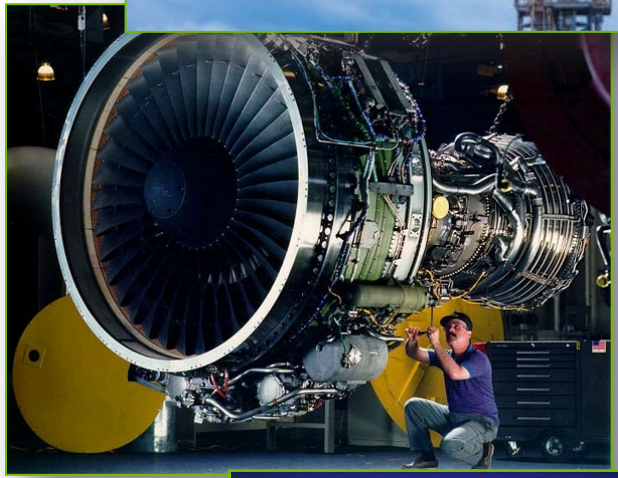
PROTECTION FOR HT – ALLOYS: MOTIVATION

Protection layer on MCrAlY

- **MCrAlY** alloys are used in high temperature (*T* > 500 °C) environment with M = Fe, Ni, Co
- These alloys form Al_2O_3 based coatings upon HT exposure (alumina formers) → **diffusion barrier for oxygen** and slowing down corrosion

But

- Al concentration in the alloy governs the formation of the protective alumina coating: if the **Al content is too low → no film formation or upkeep** of film
- Only the final α-Al_2O_3 acts as protection layer. Metastable γ-Al_2O_3 or θ-Al_2O_3 form during heat-up and result in cracks and voids caused by the phase transitions.



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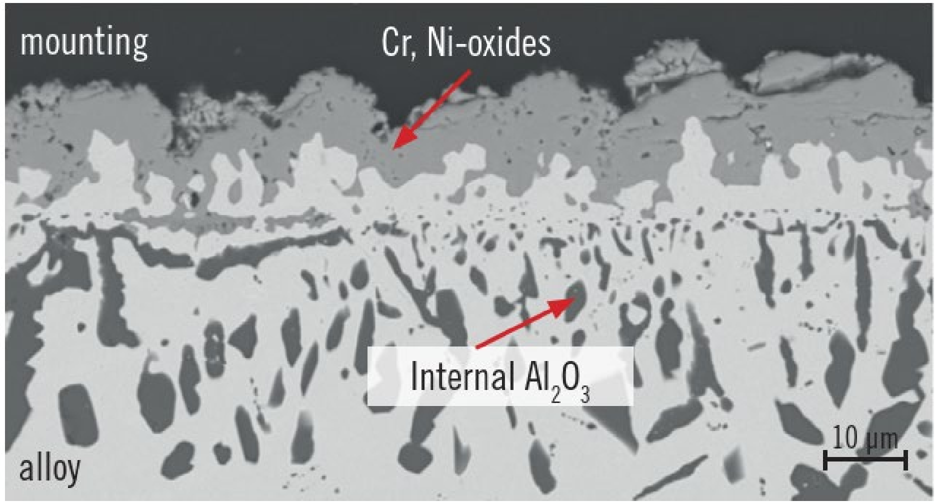
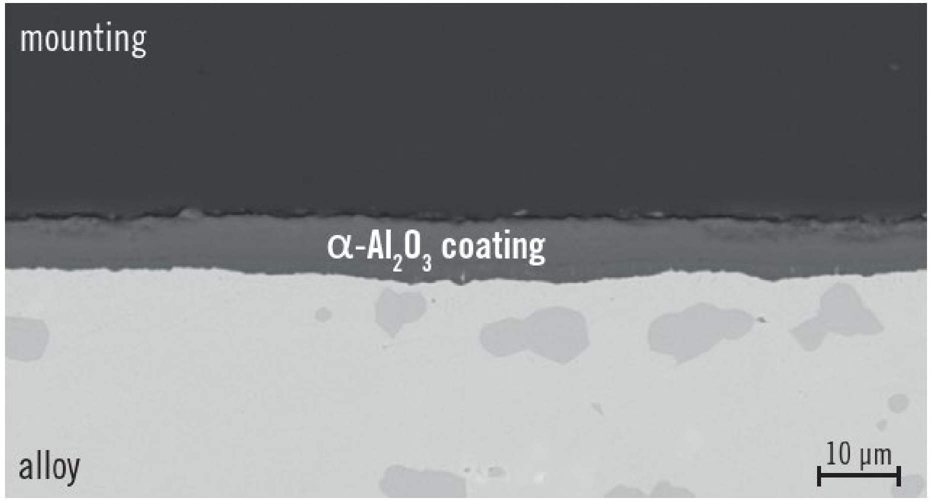
PROTECTION FOR HT – ALLOYS: SOLUTION

Coating process

- Alloy 602 (marginal alumina former – $NiCr_{25}FeAlY$) was coated with 5 µm α-Al_2O_3 by AD
- Uncoated Alloy 602 and AD-Al_2O_3 Alloy 602 were exposed to ambient air at 1000 °C for 1000 h
- Conventional Alloy 602 shows formation of Cr, Ni-oxides on the alloy surface and Al_2O_3 precipitates in the inner oxidation zone
- AD-Al_2O_3 coated Alloy 602 shows no microstructural change, voids or precipitates after heat treatment
  No oxidation occurred → very good protective character of AD-Al_2O_3 layer



Uncoated sample



α-Al_2O_3 coated sample

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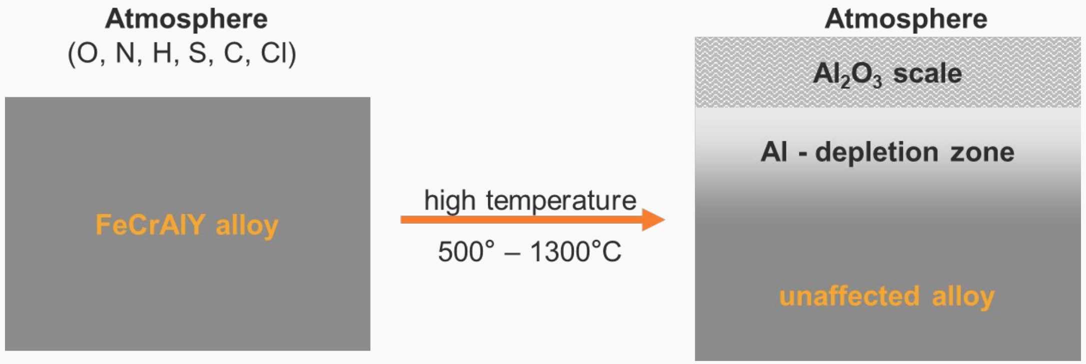
PROTECTION FOR HT–ALLOYS: EXPLANATION

AD α-Al_2O_3 enhances lifetime of components

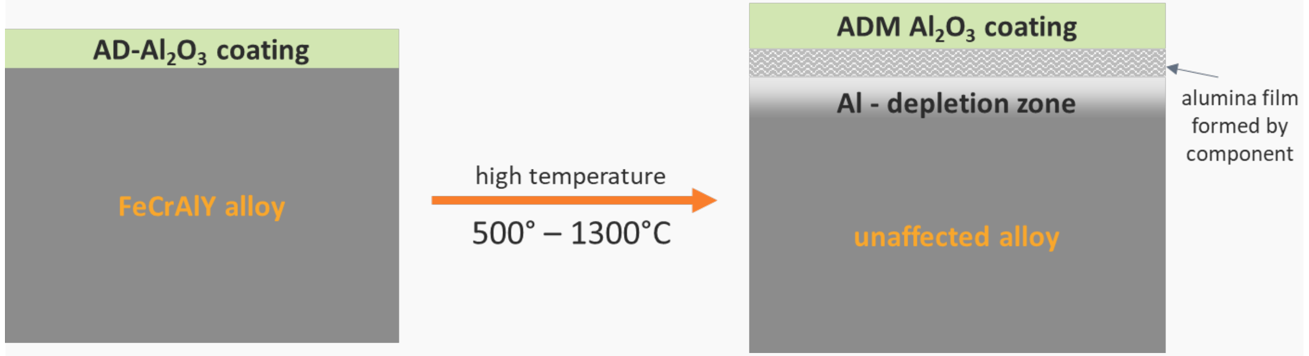
1) **Parts are protected** from the start of operation
2) Al content needed to form or sustain the alumina film formed by component is significantly reduced

→ **Thin components** with limited Al reservoirs can withstand high temperatures with extended operation times

No coating



AD-Al_2O_3 Coating



THANK YOU FOR YOUR ATTENTION

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