PROJECT FINAL REPORT

Grant Agreement number: NMP3-LA-2008-211329

Project acronym: PARTICOAT

Project title: New multipurpose coating systems based on novel particle technology for extreme environments at high temperatures

Funding Scheme: Collaborative Project, Large-Scale Integrating Project

Period covered: **from** 01.11.2008 **to** 31.10.2012

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Project website Fehler! Textmarke nicht definiert. **address:** www.particoat.eu

[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

4.1 Final publishable summary report

4.1.3 Description of the main S&T results/foregrounds

WP1 – Industrial specifications

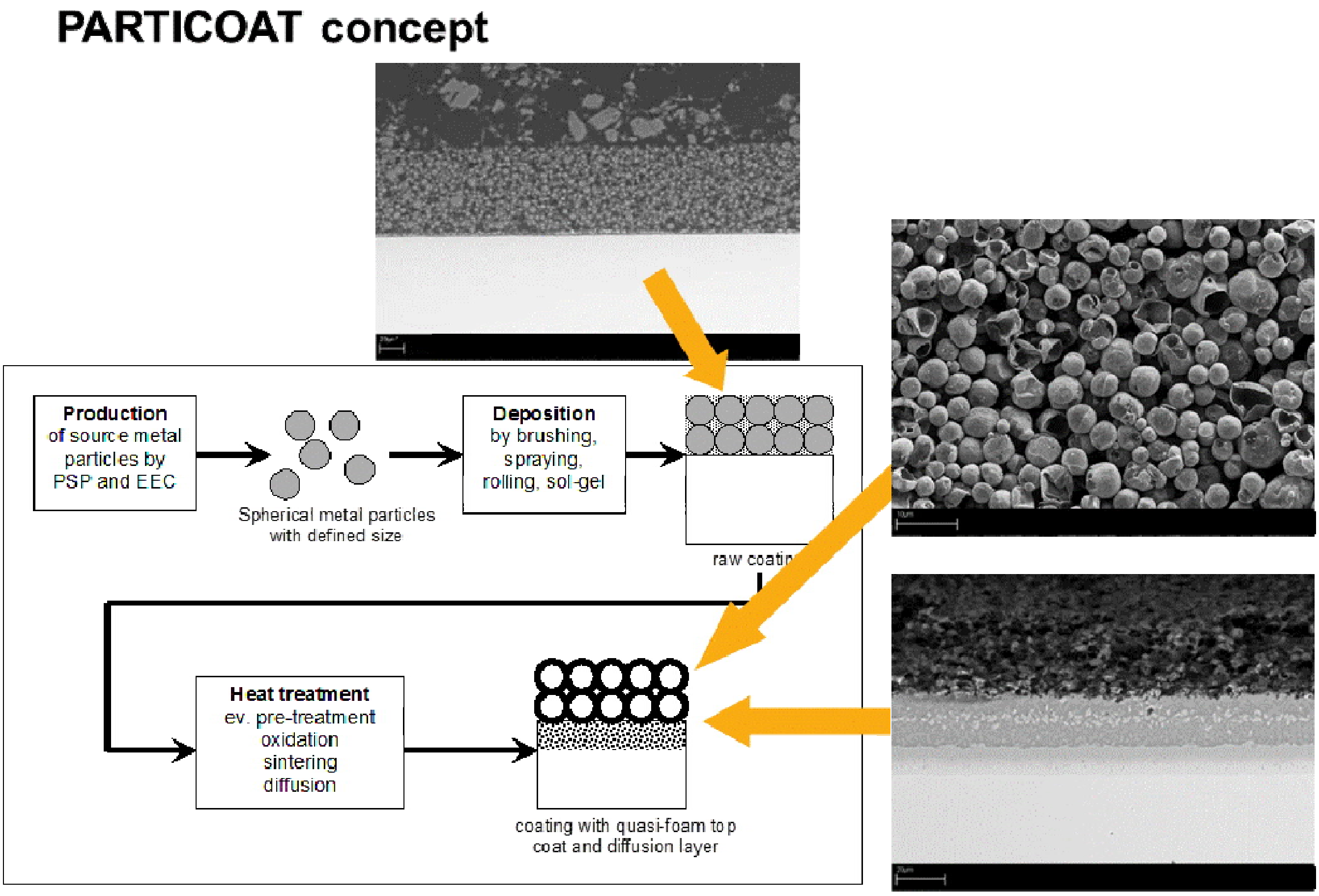
Selection of materials:

SP1 – High temperature protection
Model Alloys: *Ni, Ni20Cr*
Ni-based alloys: *IN738, PWA 1483, CM247, N5*
Fe-based alloys: *Alloy 321, Alloy 347, Alloy 446, X20CrMoV12.1*

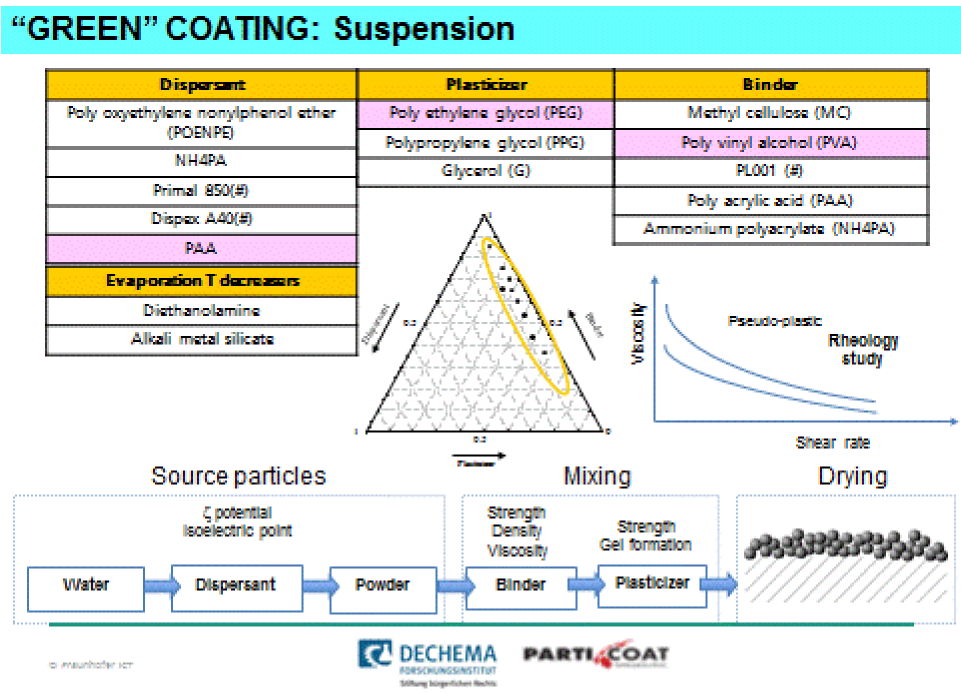
SP2 – Fire protection
Composite for construction

SP3 – Electrical insulation at high temperatures
Electrolytic pure copper

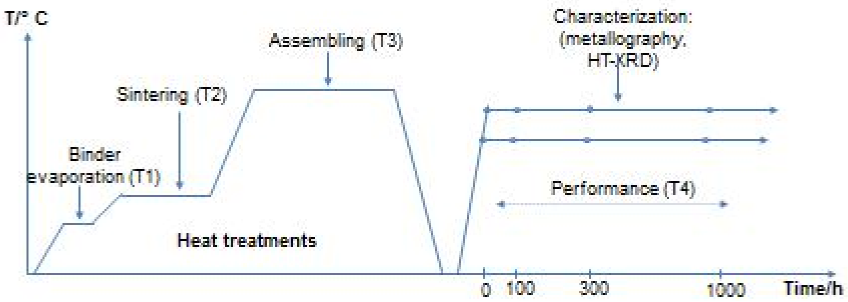
WP2 – Coating design for high temperature protection



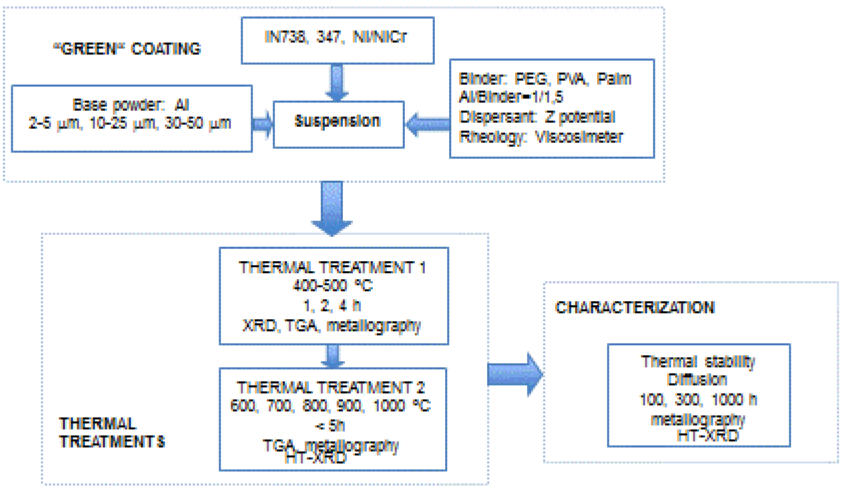
Development of suspensions for the PARTICOAT slurry:



Thermal treatment



Work flow chart for the PARTICOAT design

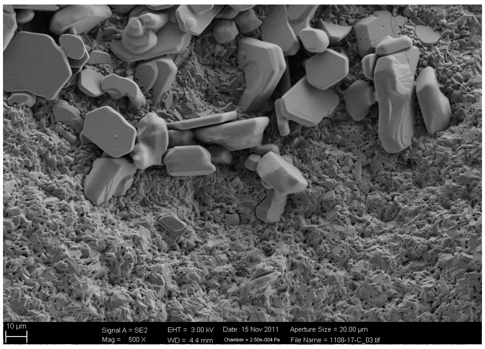


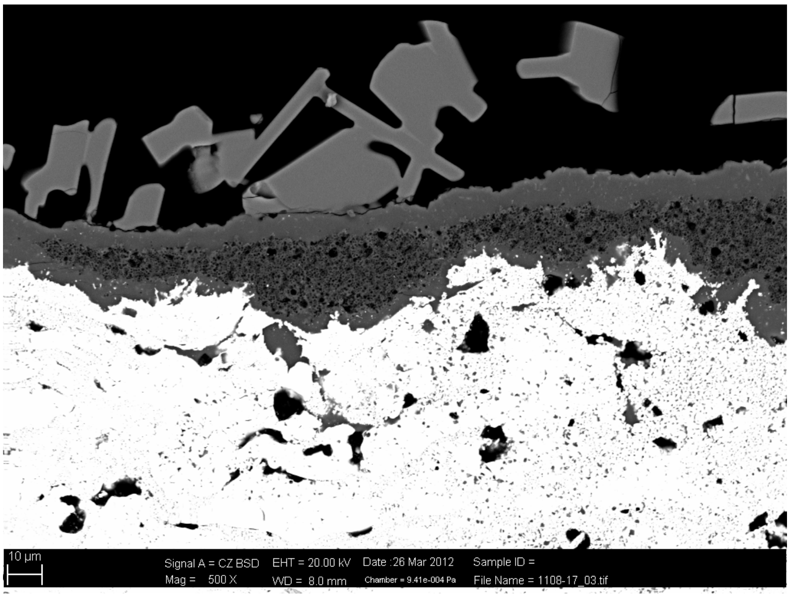
Designs for special applications – graded structures and surface sealing

Gas turbine

- TBC sacrificial coating from µm/nano-Al_2O_3

Sacrificial coating to protect conventional TBCs from YSZ against CMAS: After 50 h at 1240°C, surface and cross-section.

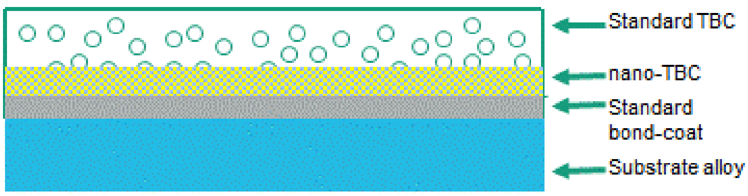




Gas turbine

- Interface between TBC and BC from nano-YSZ (grades structures)

Gas turbine: Interface between TBC and BC from nano-YSZ

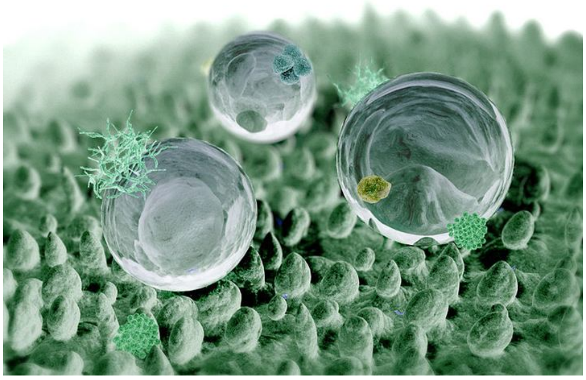


- Increase the life time of TBC by preventing crack formation
- Modification of the TBC: agglomerated nano-YPZ and nano-MgPZ
- Comparison with the state of the art

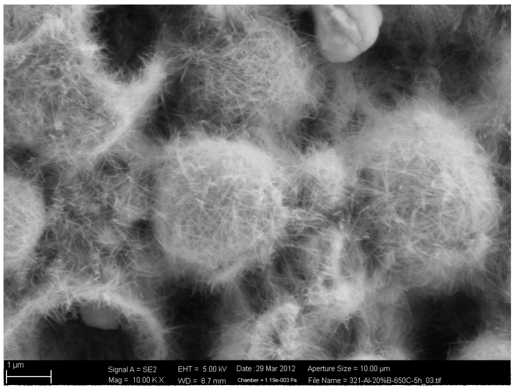
Turbocoating SIEMENS PARTICOAT Fraunhofer ICT

Antiadhesive surfaces

- Surface structures to reduce the adhesion of deposits



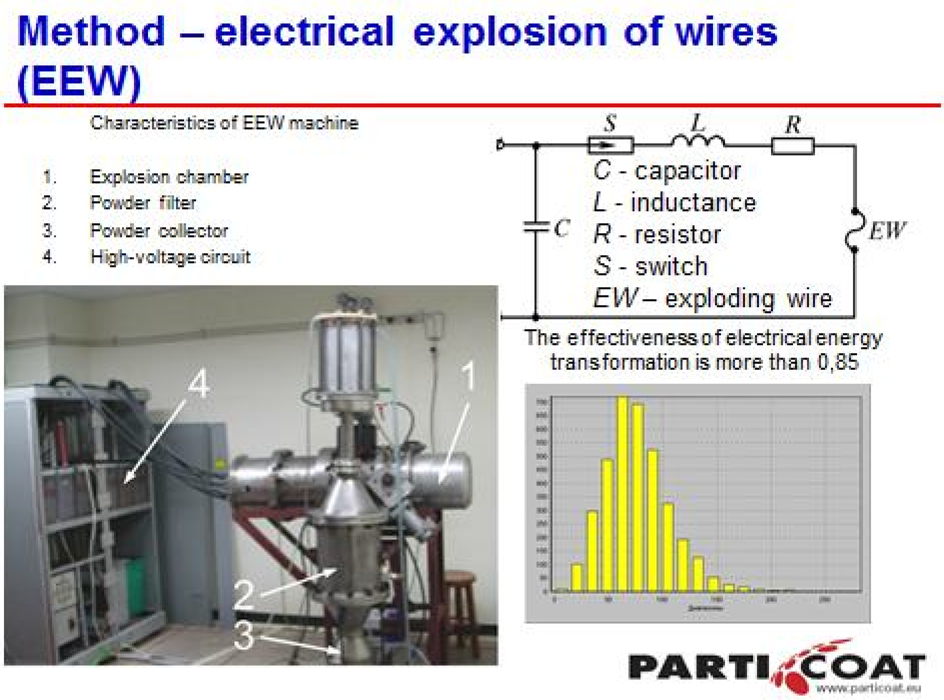
Lotus leaf

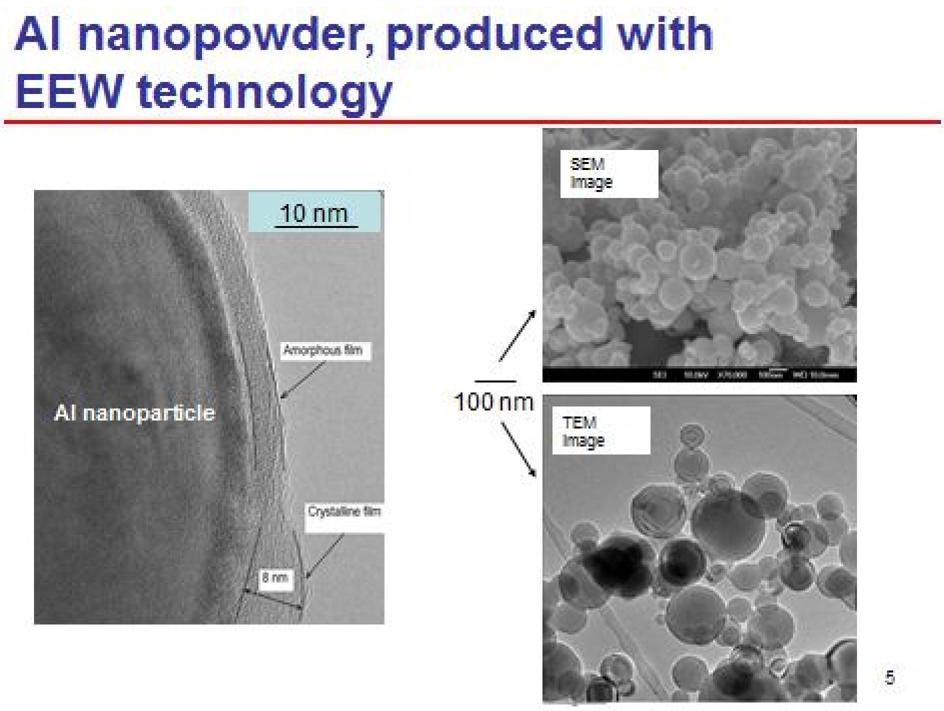


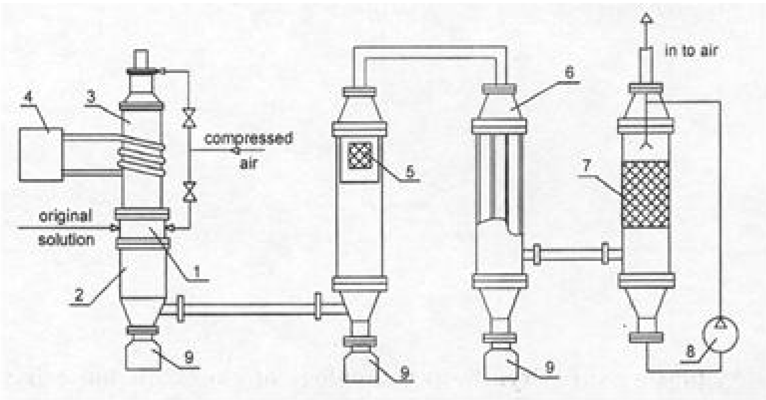
Nano-structured surface of Alloy 321 coated and heat treated, addition of boron

WP3 – Source particle production

The source particles were all produced by Sibthermochim in Tomsk, Russia







The scheme of plasma-spray equipment for synthesis of nano-powders:
1 – diers; 2 – reactor; 3 – plasma generator; 4 – high-frequency generator; 5 – filter; 6 – condensor; 7 – scrubber; 8 – water pump; 9 – containers for powders.

Main advantages:
- a very uniform distribution of components;
- nano-sized powders;
- rapidly cooled powders;
- a high energy stored in powders.

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Submicron and nanosized powders are produced on Sibtermochim equipment. These are complex pneumatic devices for grinding, classification in sizes, mixing, systems for dust collecting etc.

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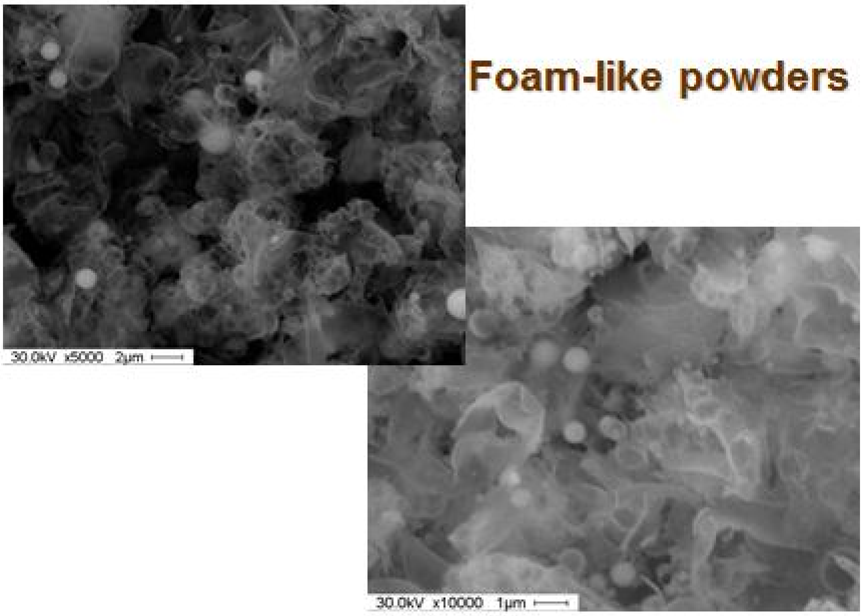
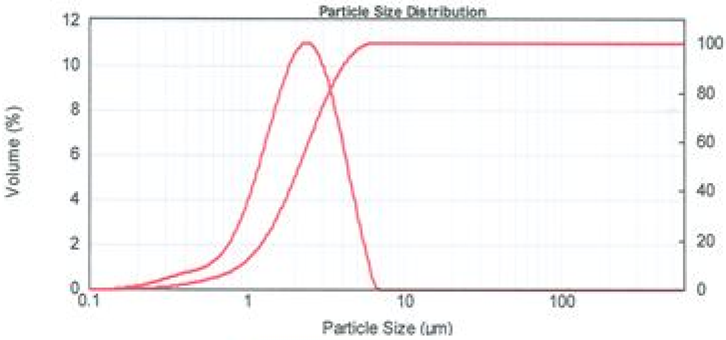
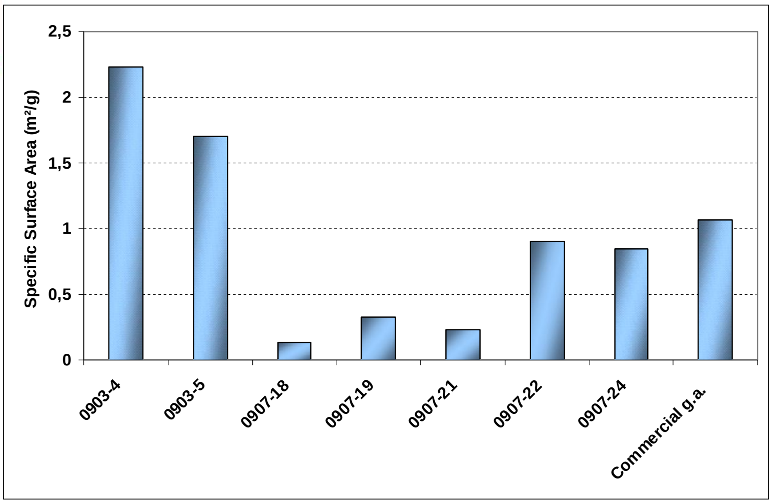


SIEVE SIZE: 0903-4



D10 = 0.92 µm
D50 = 2.14 µm
D90 = 4.01 µm

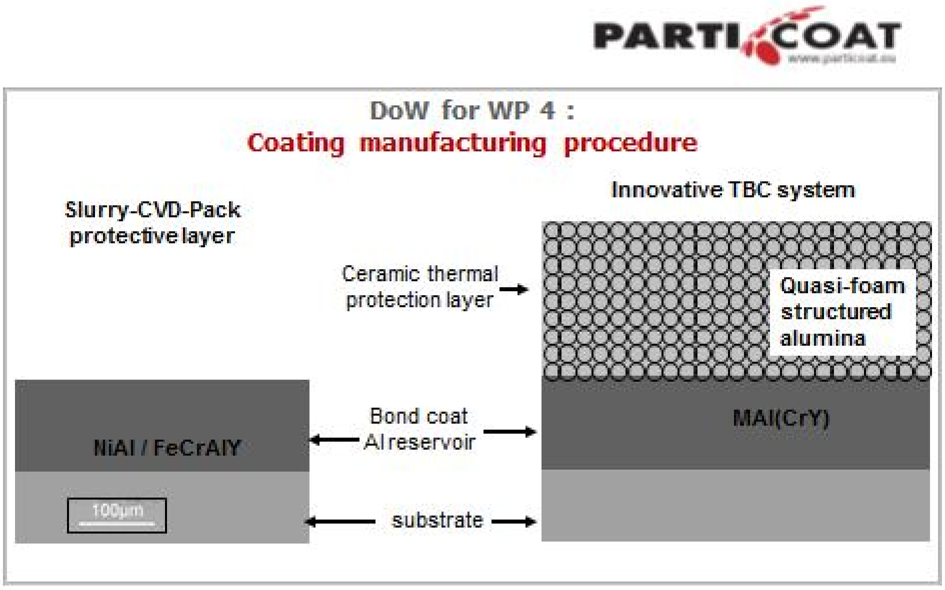
Specifif surface area:

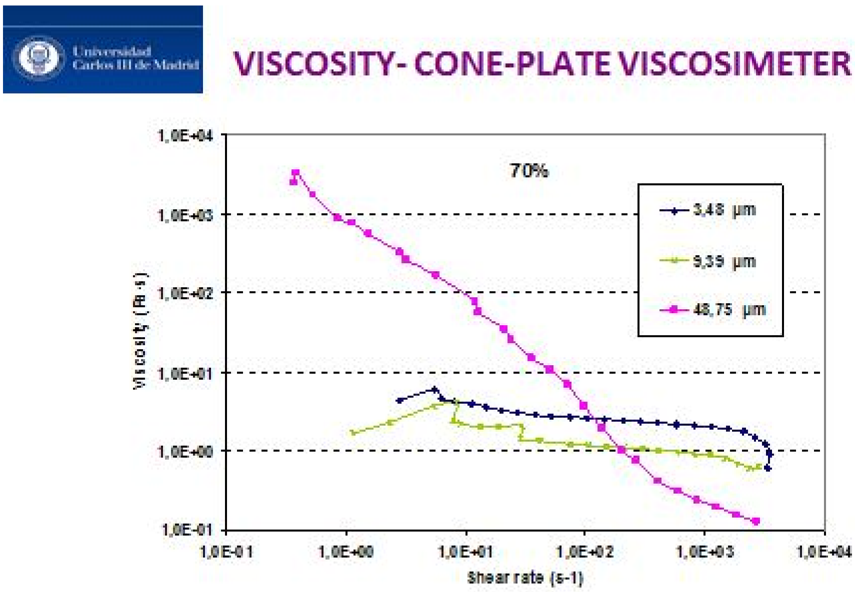


Other aluminium sources:

Atlantic Equipment Engineers - Micronmetals. (United States)
www.micronmetals.com
Valimet Inc. (United States)
www.valimet.com
Aluminium Powder Company (Alpoco). (United Kingdom)
www.alpoco.com
Sulzer Metco.
Alcoa

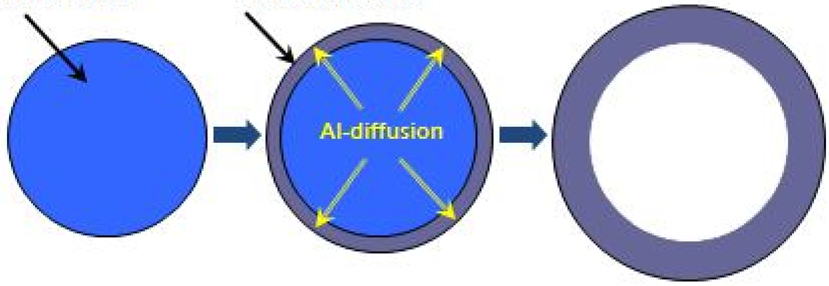
WP4 – Coating manufacturing procedure





Influence of aluminium particle size and shape

Oxidation of micro-sized spherical aluminium particles studied in situ by high temperature X-ray diffraction



Oxidation of metallic aluminium nano/micro particles into hollow aluminium oxide spheres

Nano / micro size = low amount of grain boundaries

Aluminum = very creep ductile, i. e. adherence to oxide maintained during conversion

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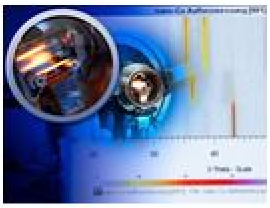
Investigated particles and experiments



High temperature X-ray diffraction

Heating in air

Al 31% <5 µm 61% 5-10 µm, powder on Pt-holder (0903-4)	RT – 1300°C, ΔT=25°C
Al 31% <5 µm 61% 5-10 µm + PEG on Aluchrom Y Hf (0903-4)	400°C – 1200°C, ΔT=25°C
Al 0.3 – 0.7 µm + PEG on Aluchrom Y Hf	RT – 1100°C, ΔT=25°C
Al 2 – 5 µm + PEG on Aluchrom Y Hf (0811-19)	400°C – 1200°C, ΔT=25°C
Al 30 – 50 µm + PEG on Aluchrom Y Hf	RT – 1350°C, ΔT=50°C

Isothermal in air

Al 31% <5 µm 61% 5-10 µm + PEG on Aluchrom Y Hf (0903-4)	3 h at 650°C, 850°C, 1000°C
Al 31% <5 µm 61% 5-10 µm + PEG on Aluchrom Y Hf (0903-4)	24 h 800°C

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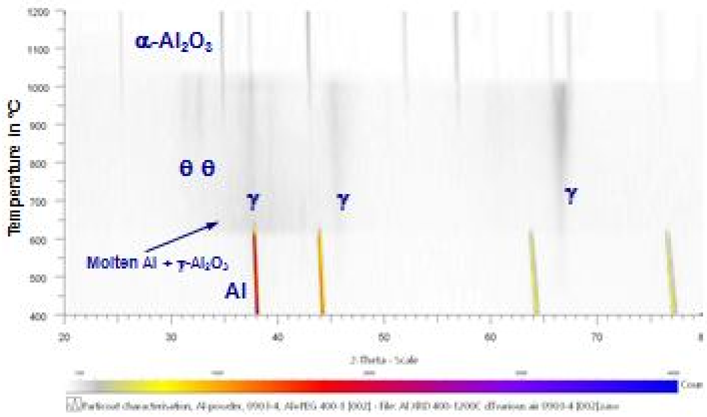
(0903-4) Al 31% <5 µm, 69% 5-10 µm + PEG on Aluchrom Y Hf



Series of X-ray diffraction patterns on heating from 400° C to 1200° C in top view

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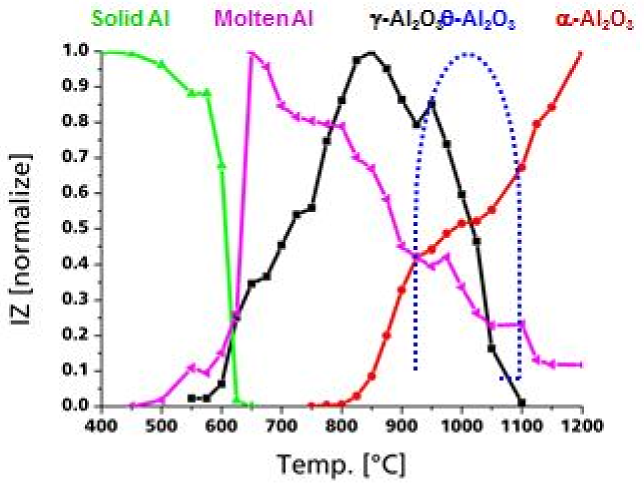
(0811-19) Aluminum 2-5 µm + PEG on Aluchrom Y Hf



Intensity curves iz(T) from high temperature X-ray diffraction on heating from 400° C to 1200° C

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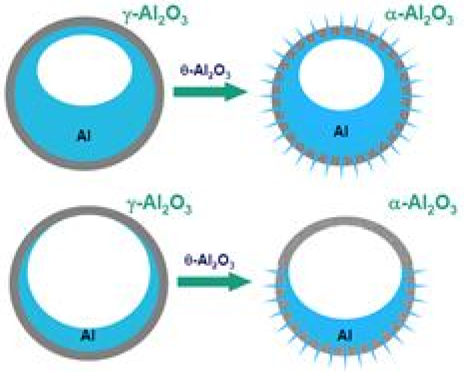
Oxidation mechanism of nano- and μ-Al particles

Transformation γ-Al_2O_3 → α-Al_2O_3 above 850°C



High disorder structure, cubic-fcc

Ordered structure, hexagonal close packed oxigen lattice
Higher atomic density
Volume shrinkage about 13,8 %

→ Formation of nano-cracks and pores → liquid Al penetrates the scale and oxidises

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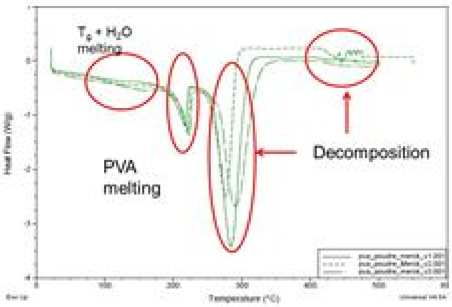
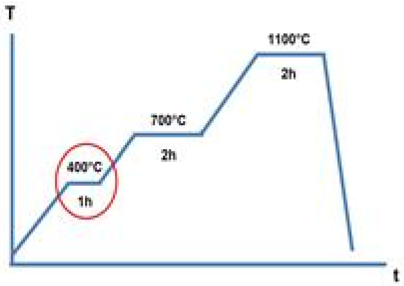
Tailoring the heat treatment

Example: slurry made of H_2O + 1%PVA+ 45 wt. % Al micro-particles

Decomposition of slurry + followed by sintering + diffusion + oxidation





400°C / 1h + 700°C / 2h + 1100°C / 2h (Ar)*

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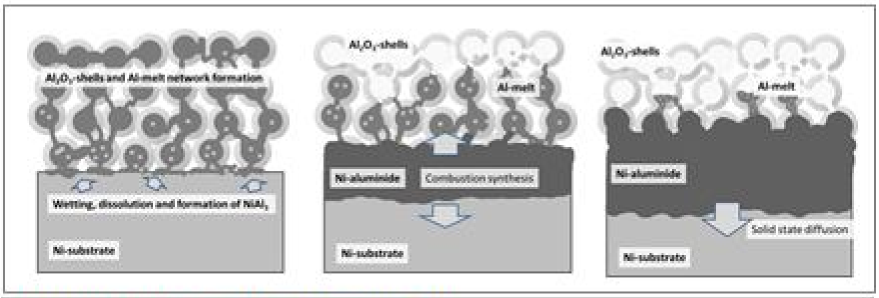
Mechanisms of formation of PARTICOAT coatings



1) Wetting of the surface by molten Al
2) Dissolution of Ni into molten Al: combustion synthesis (heat released)
3) Solid-state diffusion + breakdown of spheres

→THESE MECHANISMS WILL APPLY ONTO ALL THE SUBSTRATES (WHETHER IRON OR NICKEL-BASED) DEPENDING ON THEIR COMPOSITION
→THESE MECHANISMS ALSO APPLY REGARDLESS OF THE COMPOSITION OF THE SLURRIES (DOPING OF Al PARTICLES)

IRON BASED ALLOYS

Main methodology of investigation:

→ Materials: AISI 321, AISI 446, AISI347, A310S, X20CrMoV12.1, 16Mo3

→ Composition of solution: combinations of Al/B, different sizes of Al particles (single + multiple), Al/Si, Al/Ni

→ Method: spraying (aerograph), brushing & dipping

→ Tailored heat treatment (HT) to manufacture coatings in a quick and reliable manner

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µm-Al + B

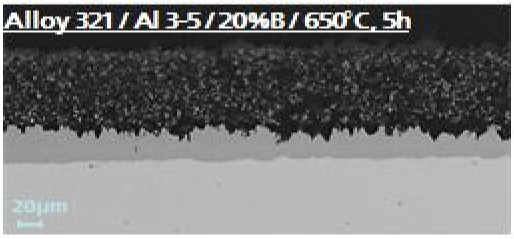
Single size 3-5 µm Al
0% / 10% / 20% B

Increase in the B% :

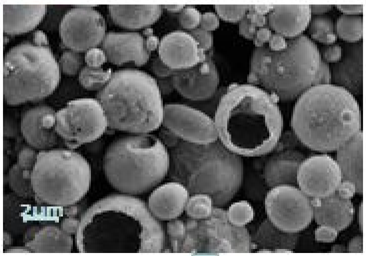
- ↑ Sintering and compaction.
- ↑ Formation of whiskers of borate
- ↑ Adherence of the top coat
- ↑ Ductility of the diffusion layers

Multiple size 1-20 µm Al
+ 20% B

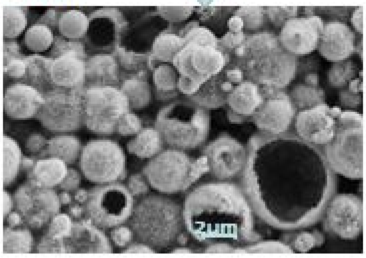
→ Similar results



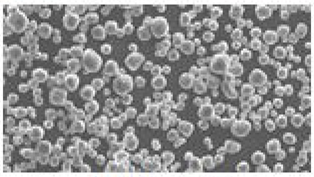
0%B



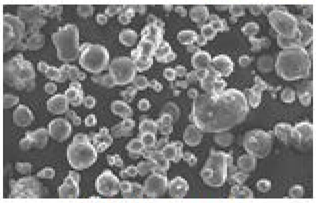
20%B



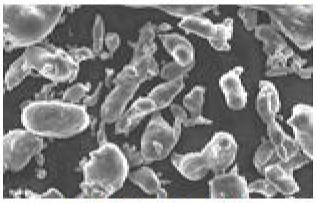
Mixing Al with something else…Al/Ni, Al/Si, multiple size vs. single size



Single size Al
With and without Ni

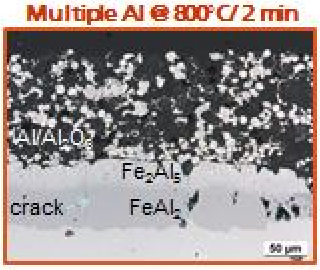


Multiple size Al

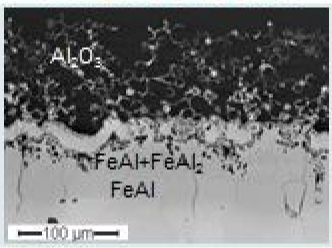


Multiple size Al-Si

Multiple Al @ 800°C/ 2 min



Multiple Al @ 800°C/24 h



Increasing time allows to obtain the oxidised hollow spheres top coat + Fe-rich aluminides (less brittle)

NICKEL-BASED ALLOYS

Main methodology of investigation:

→ Materials: Pure Ni, Ni20Cr, IN-738LC, PWA-1483, CM-247, N5 (aero)

→ Composition of the water-based slurry: different sizes of Al particles (single + multiple), combinations of Al/B, Al/Si, Al/Pt, Al/RE...

→ Method: spraying (aerograph) & brushing

→ Tailored heat treatment (HT) to manufacture coatings in a quick and reliable manner

→ Input of thermodynamic calculations using ThermoCalc ® software: appearance of phases / effect of substrate composition

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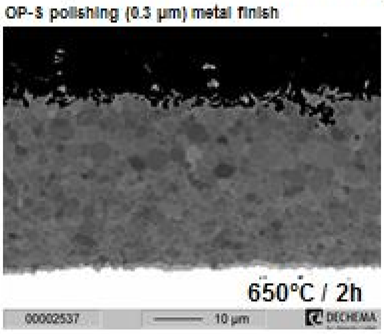
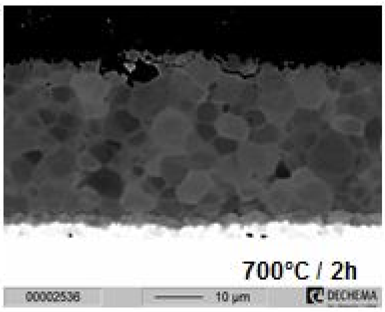
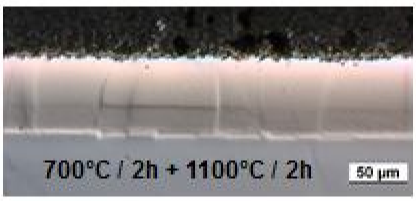
Pure nickel as model substrate

Aluminization onto pure Ni: influence of the temperature

OP-S polishing (0.3 µm) metal finish







→ Higher grain size evidenced @ 700°C

→ From 3 µm to 6µm on average

→ Columnar grains after full TT

Need of tailoring in superalloys: thermodynamics

7

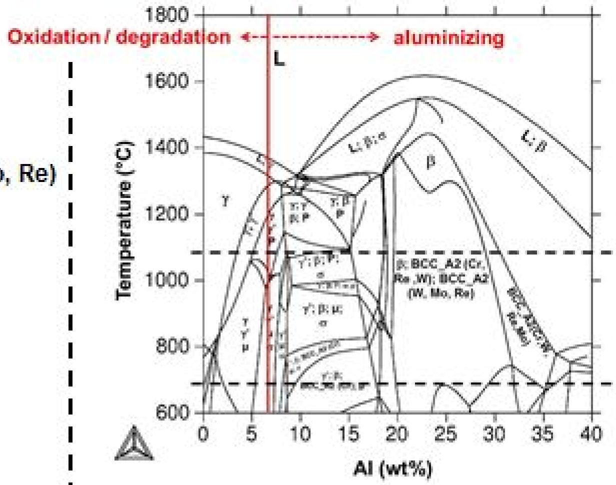
Cr content +

N5

<u>Modeling</u>

→ β-NiAl

→ Precipitates (Cr, W, Mo, Re)



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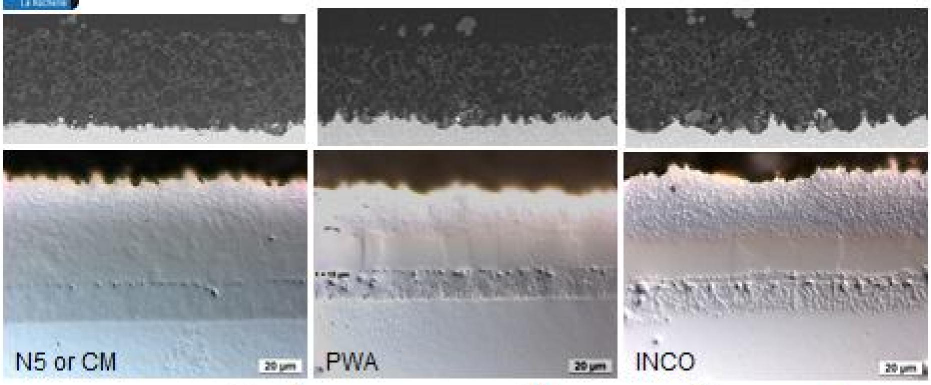
Superalloys and 6 µm Al particles



7 8 12 16

Cr content +

N5 CM PWA INCO

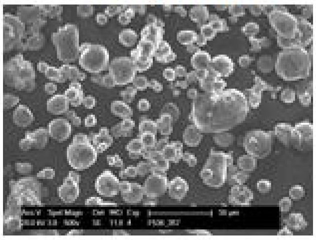
Evolution of the microstructure of the coatings with the Cr content

→ From small equiaxed grains (N5 / CM) to inner columnar grains (PWA/INCO)

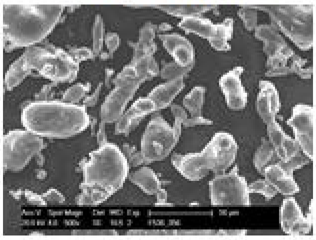
→ Precipitates mostly at the outermost additive layer (low solubility)

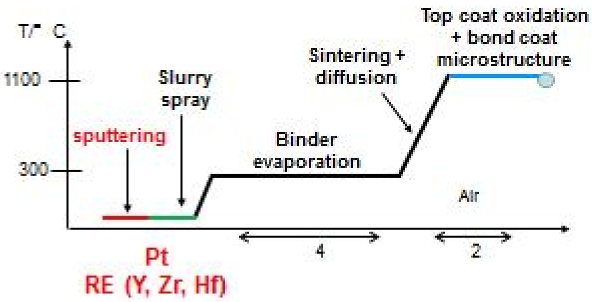
Mixing Al with something else…
case of Al/X (Si, Pt, RE)

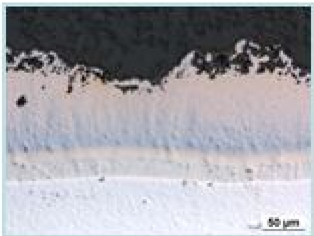
Multiple size Al



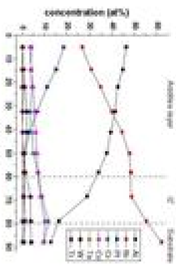
Multiple size Al-Si

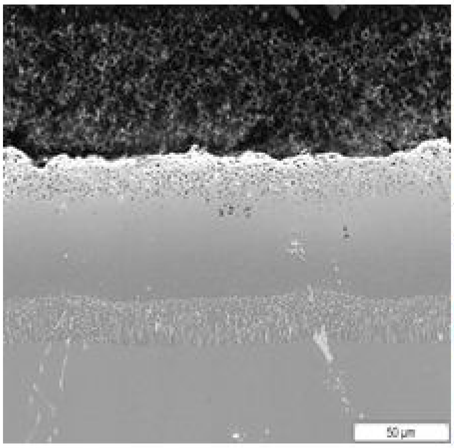




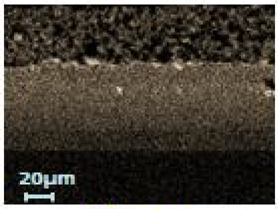


Platinum-modified PARTICOAT

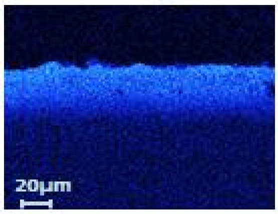




Al map



Pt map

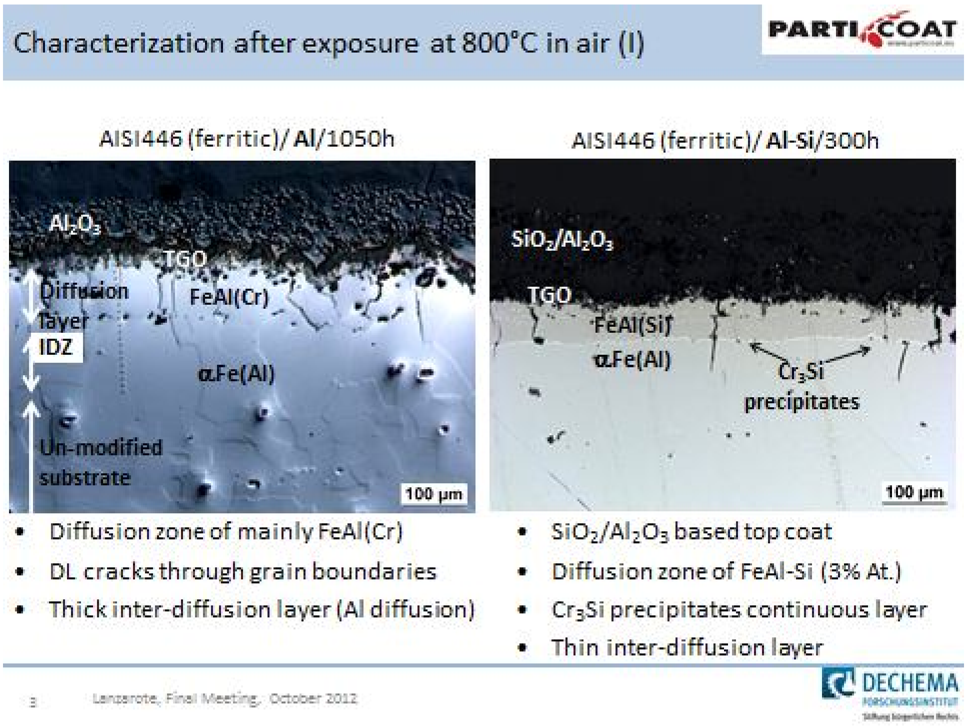


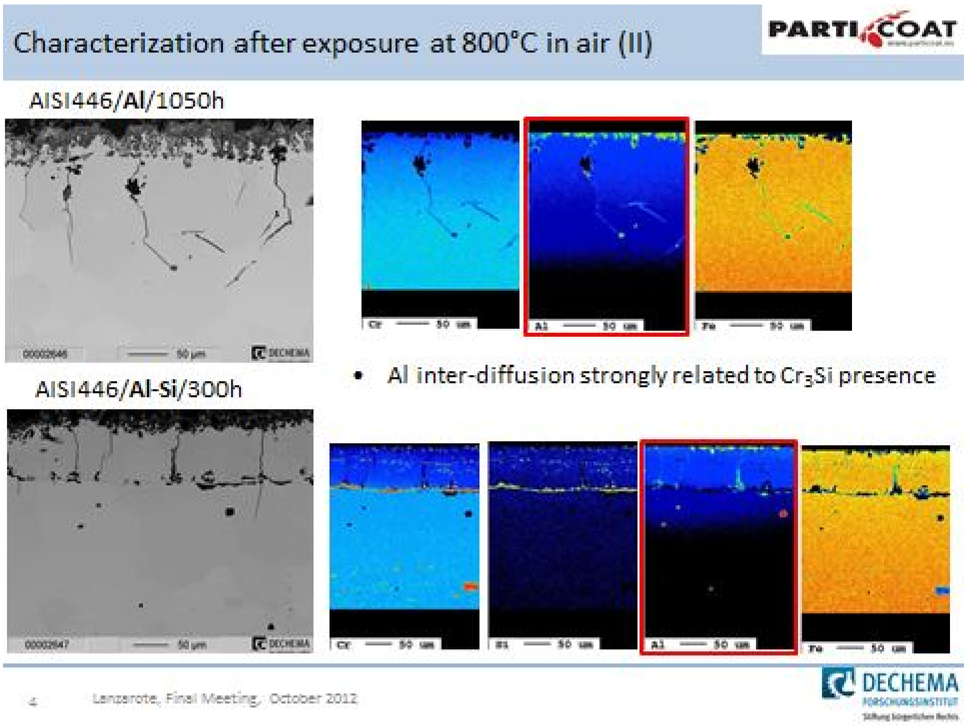
→ Top coat + (Ni,Pt)Al additive layer + very thin interdiffusion layer
→ Expected to increase further oxidation & corrosion resistance

WP5 – Performance and degradation mechanisms

WP5.1.1 Oxidation of Fe-based alloys

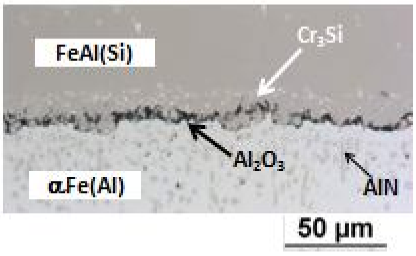
DECHEMA / DFI



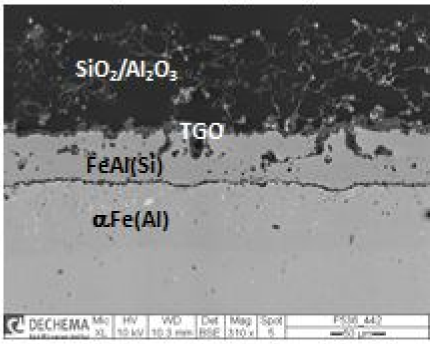


Characterization after exposure at 800°C in air (III)

AISI347 (austenitic)/ **Al-Si**/300h



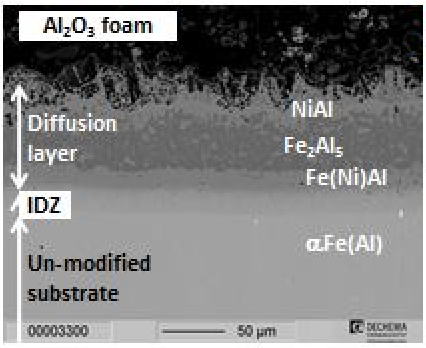
AISI347 (austenitic)/ **Al-Si**/1050h

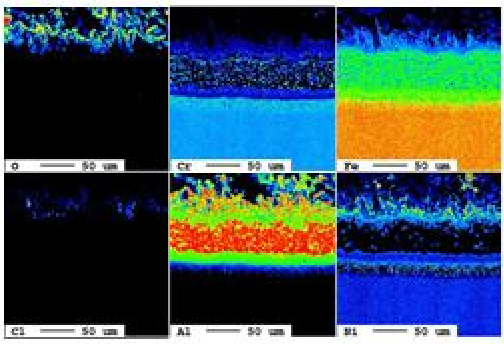


- Similar top coat thickness and composition as observed for ferritic substrates.
- TGO of Al_2O_3 similar to ferritic substrates (approx. 5 µm)
- Thinner diffusion zone as observed for ferritic substrates (50 µm vs 100 µm)
- Diffusion zone of FeAl(Si) (7% At.)
- Cr_3Si does not form a continuous layer

Characterization after 600°C

AISI347/ **Al**/1200h/$\mathbf{Cl_2}$

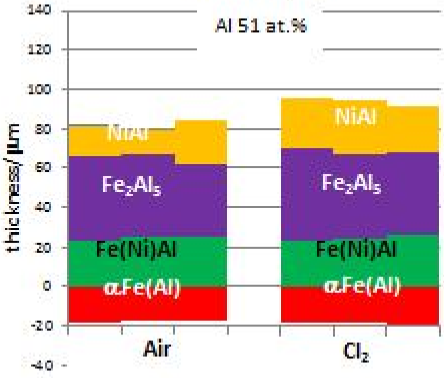




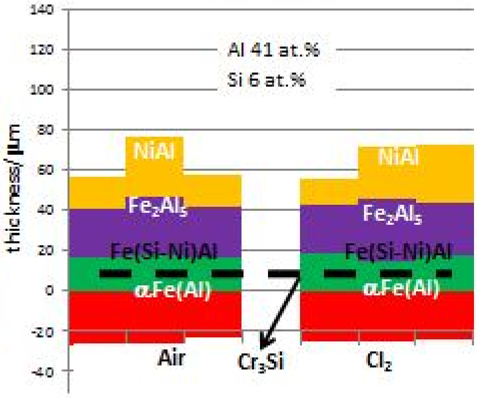
- No Chlorine species are detected in diffusion zone
- Phases present in diffusion layer are similar to those observed in exposure in air
- Demonstrates the importance of having a crack free diffusion zone

Phase evolution at 600°C

AISI347/ **Al**



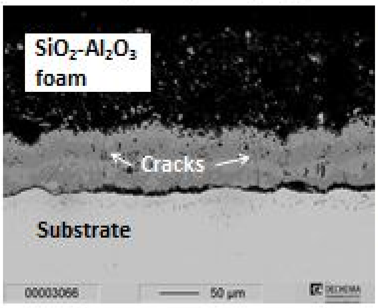
AISI347/ **Al-Si**

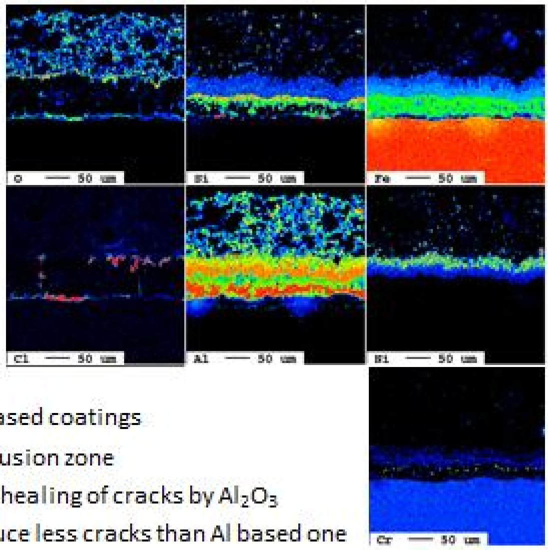


- Diffusion layer is thinner for Al-Si
- IDZ thickness increases with Si content (Si stabilizes ferritic phase)
- Al at.% does not significantly decrease during these exposure conditions and time

Characterization after 600°C

P91/ **Al-Si**/100h/Cl_2





- Diffusion layer is thicker for Al based coatings
- Chlorine species detected in diffusion zone
- Weight gain increased due to re-healing of cracks by Al_2O_3
- Al-Si based slurry coatings produce less cracks than Al based one

- Protection against corrosion:
  - Main protective problem of the coatings is related to the **cracks** in diffusion layers (CTE mismatch).
  - **Al-Si** diffusion layers show lower weight gains and lower chlorine species formation.
- Aluminium inter-diffusion:
  - At 800°C Al inter-diffusion increases strongly (reduced Al reservoir).
  - Almost no evolution observed at 600°C.
  - Ferritic substrates show higher inter-diffusion than austenitic substrates
  - Si addition decreases inter-diffusion for high Cr content ferritic substrates due to formation of **Cr_3Si** between the diffusion and inter-diffusion layer
  - Si addition increases inter-diffusion for austenitic substrates due to the stabilization effect of ferritic phase.

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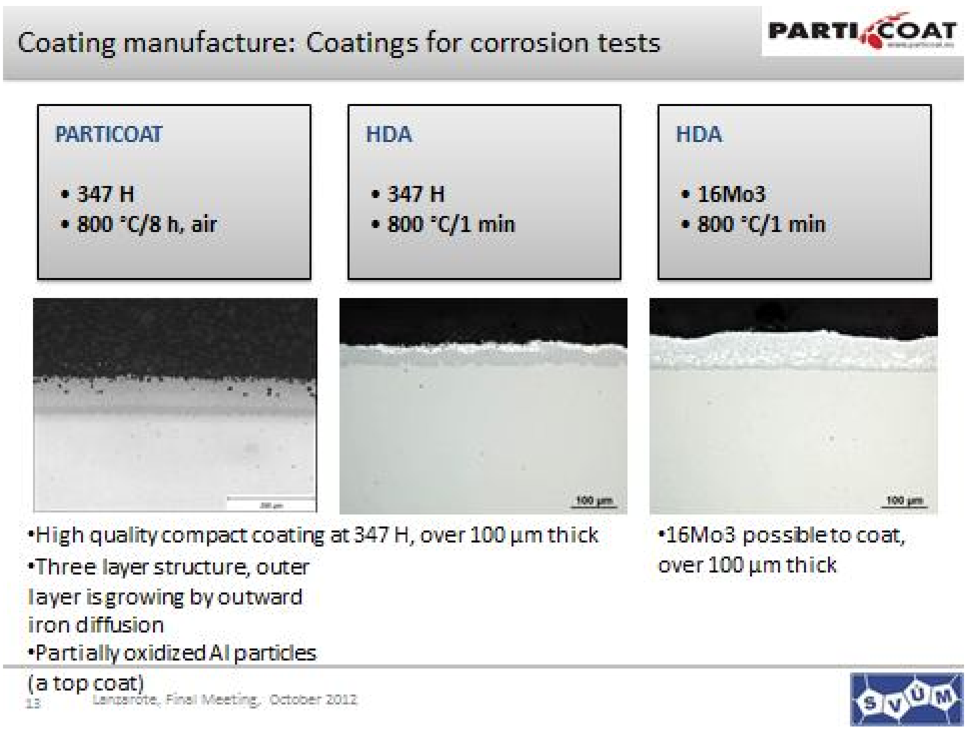
<u>SVUM</u>

Comparison PARTICOAT to Hot Dip Aluminizing

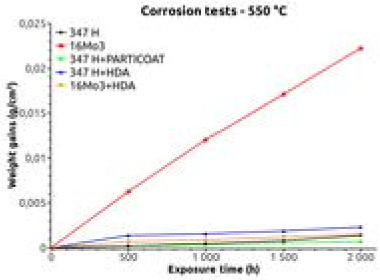
PARTICOAT
- 347 H and 16Mo3
- Surface only mechanically filed by and degreased in acetone
- Slurry: 50 % Al, 1 % PVA, 49 % H_2O
- Al particles 3 – 5 µm
- Deposition: deep coating 200 – 300 µm thick layer
- annealing: 800 °C/8 h, air

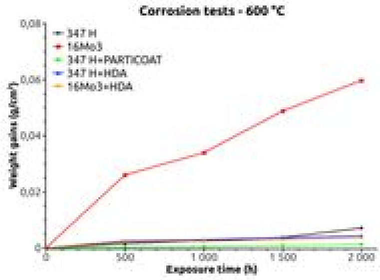
Hot Dip Aluminizing (HAD)
- dipping into molten aluminium bath
- under NaCl/KCl/NaF flux
- 800 °C/1 min

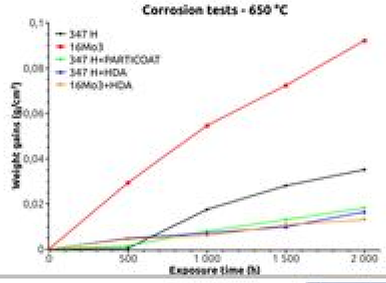


Laboratory tests – atmosphere: results

PARTICOAT





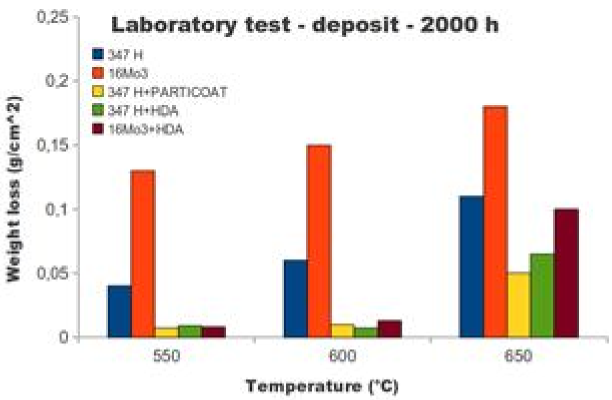


- PARTICOAT indicates very good result similar to HDA
- The coatings exhibit benefits especially at higher temperatures

Laboratory tests – deposit: results

PARTICOAT

- Weight losses evaluated (after corrosion product removing)
- All coatings indicate similar corrosion properties
- At 650 °C coaings were damaged under the deposit

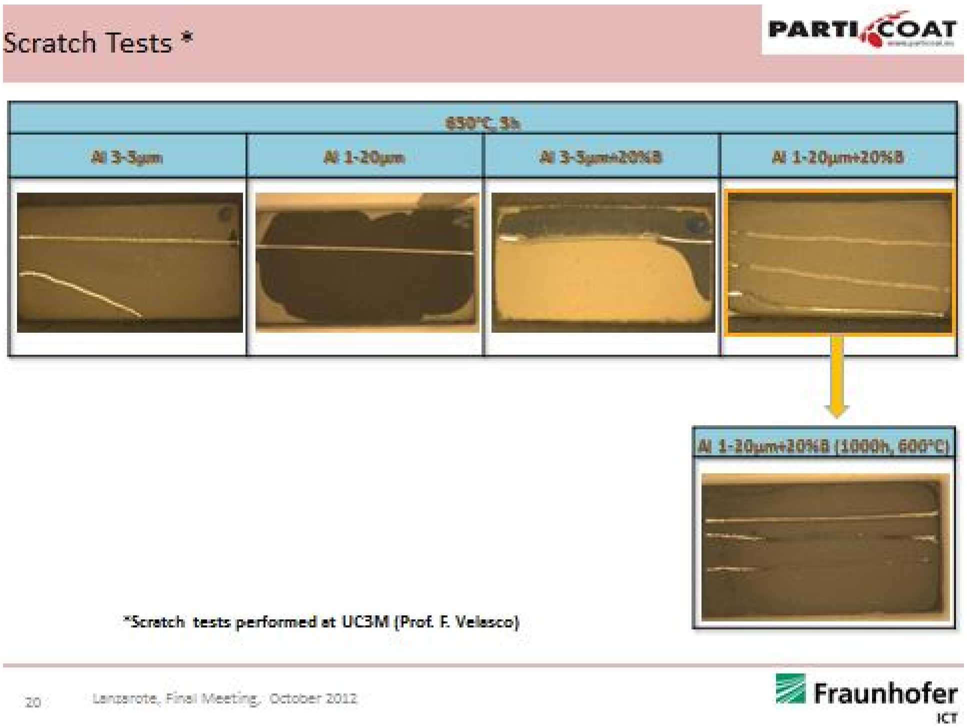


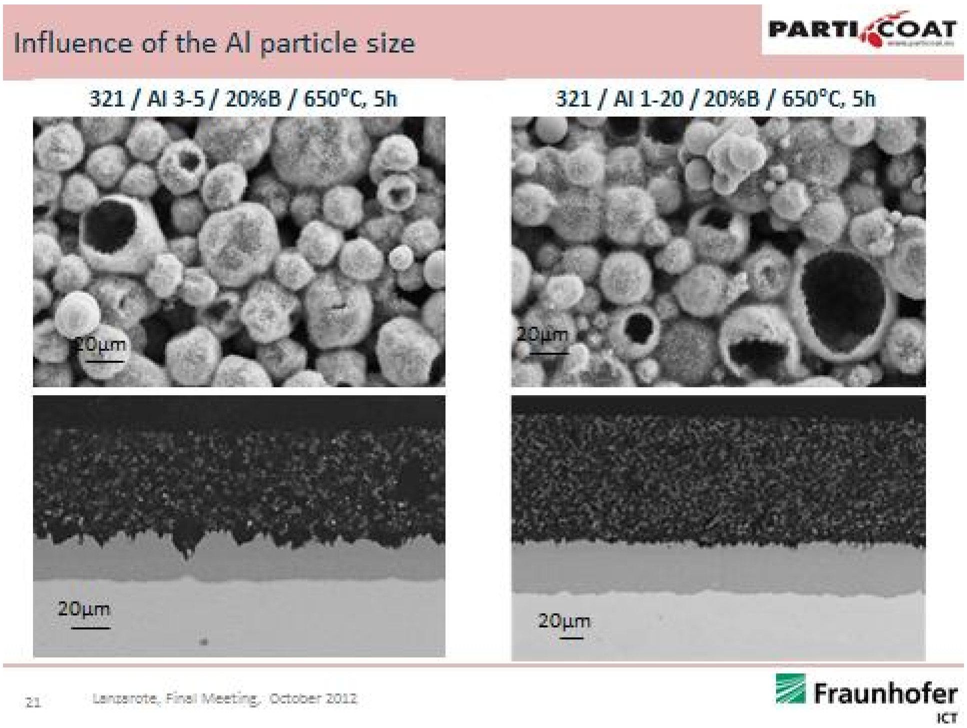
Fraunhofer ICT

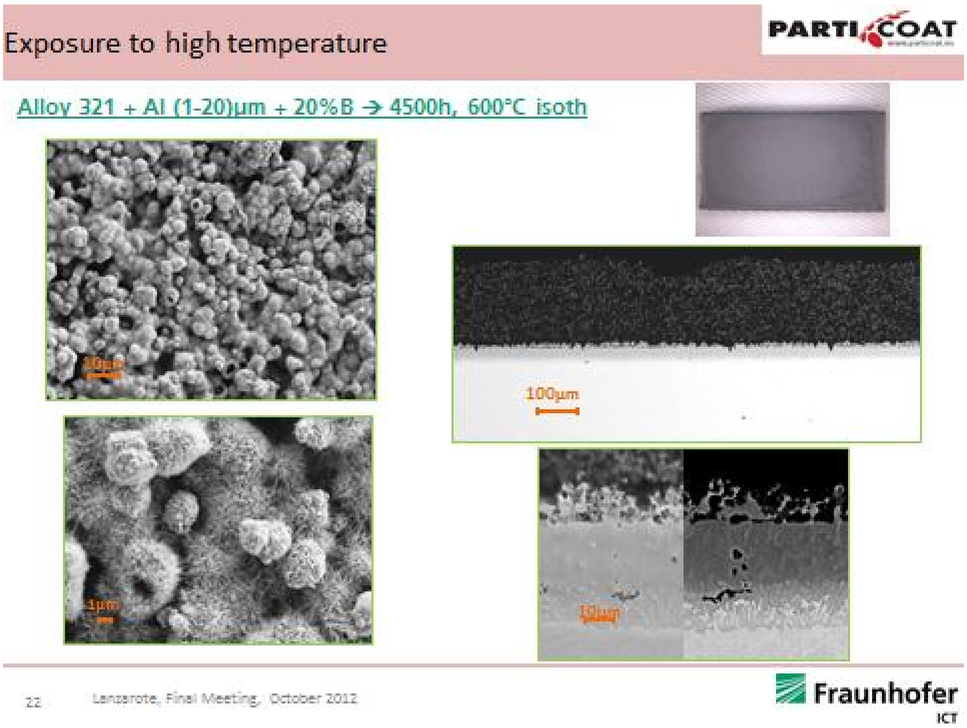
Effect of Boron addition to the Al-slurry
Influence of Boron content and particle size:

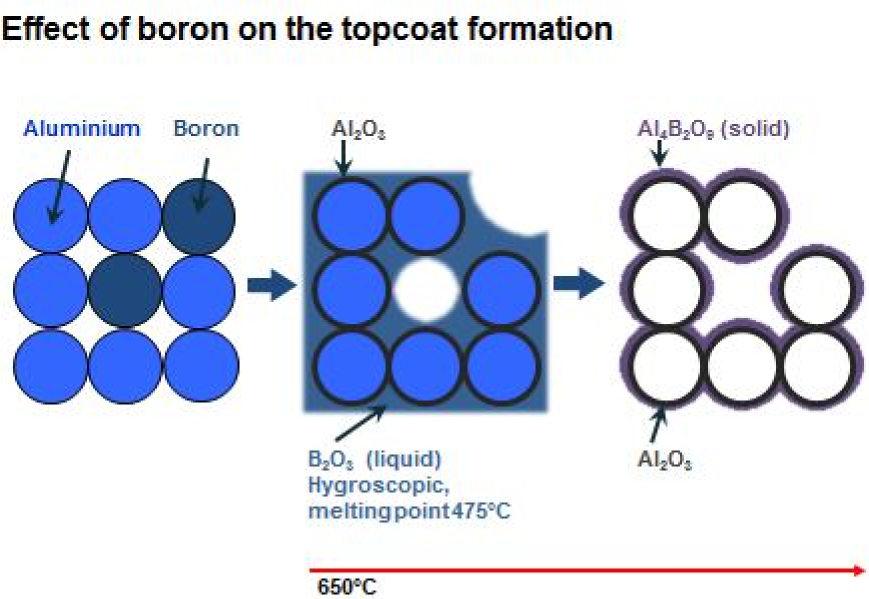
- 20%B with multi-size 1-20µm Al

Material: Alloy 321









Conclusions

- In long-term exposure, coatings produced with the following heat treatment parameters showed the best performance till 4500h.
  - Alloy 321 + Al (1-20µm) / 20%B, 650°C / 5h in air
- The multi-size 1-20µm Al powder forms top-coats with high stability and adhesion than the single sized powders.
- Boron addition improves adhesion to the substrate for austenitic steels. Boron oxide provides low temperature sintering and protect the metal against oxidation.

TECNATOM

Comparison between NDT in order to select the most suitable for in-service inspection and surveillance

- Ultrasonic test (UT)
- Eddy current test (ET)
- Interferometry

PARTICOAT

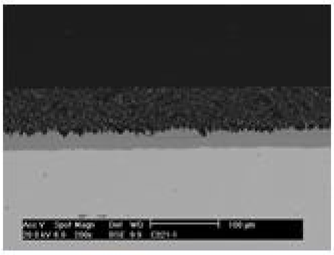
Non destructive measurement and Validation

Measurement:

Non destructive measurements by means of ET and UT

NDT results validation:

NDT results have been compared with results obtained from destructive analysis (cross section measurements)



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PARTICOAT

Conclusions

Non destructive Technique selection:

- ET is the most promising technique
- UT is not able to provide reliable results due to top coat structure (hollow spheres)

Device Selection:

- Among ET devices, Salutron has demonstrated higher accuracy and robust behavior than Positector

Coating Measurements:

- NDT measurements of the top coat (hollow spheres)
- NDT techniques are not able to measure layers beneath the top coat (diffusion layers)

Measurements validation on to Iron based alloys:

- Austenitic Stainless steels: Medium accuracy
- Ferritic steels: Very good accuracy

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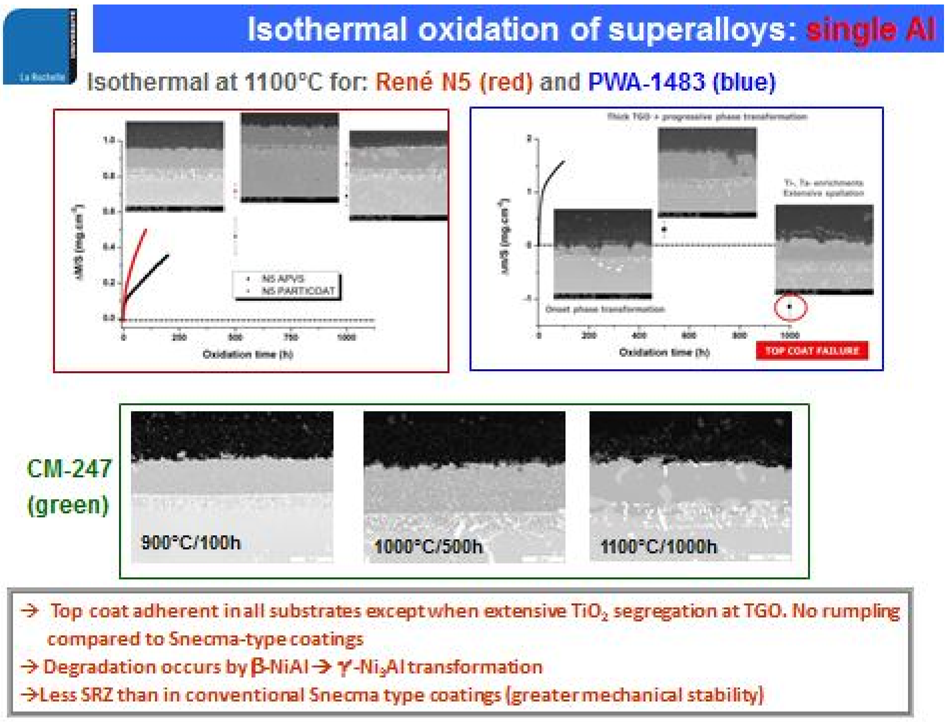
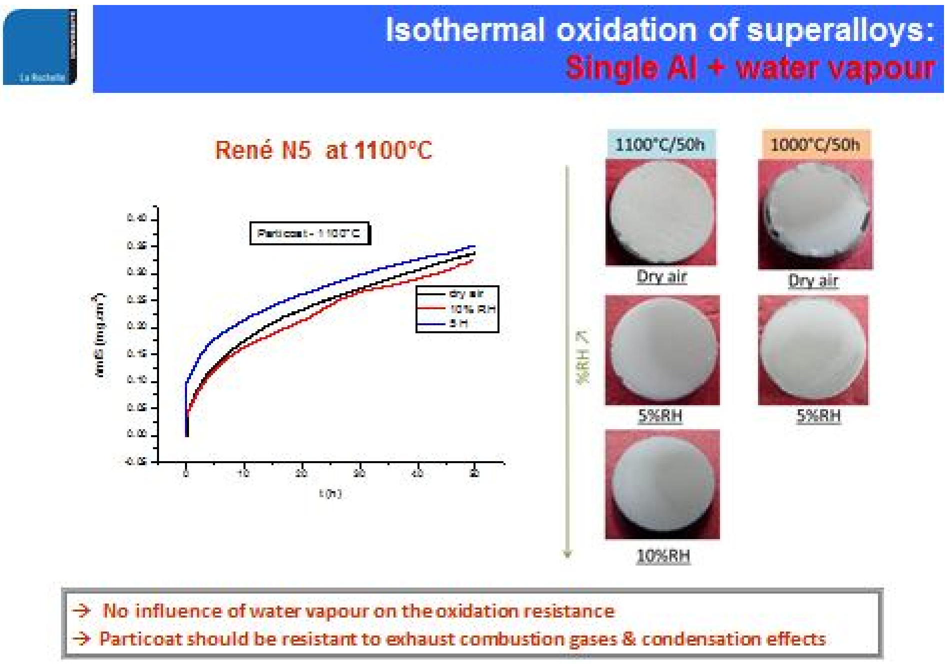
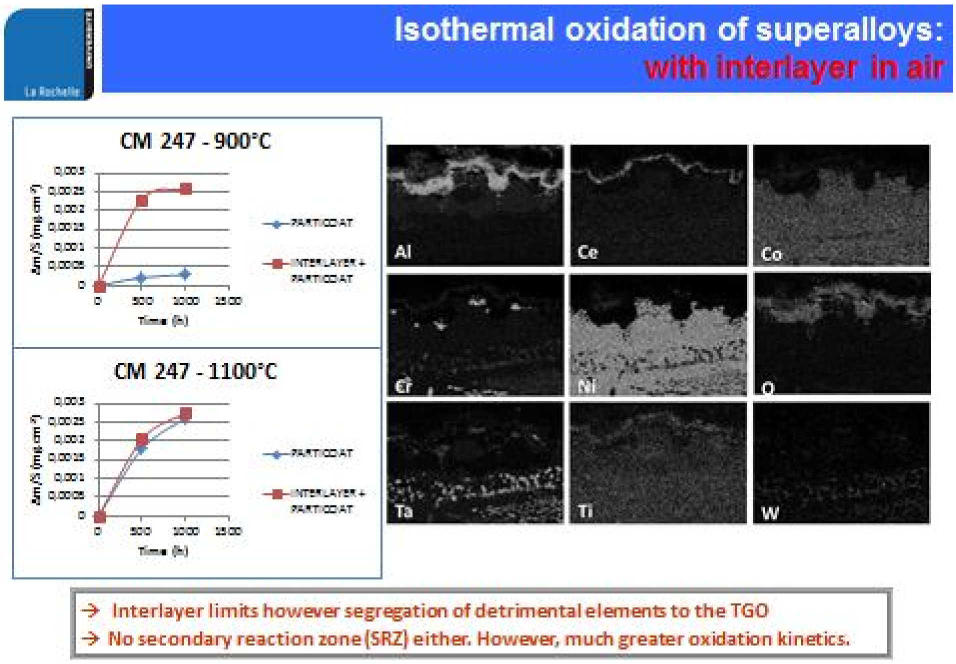
WP5.1.2 Oxidation of Ni-based alloys

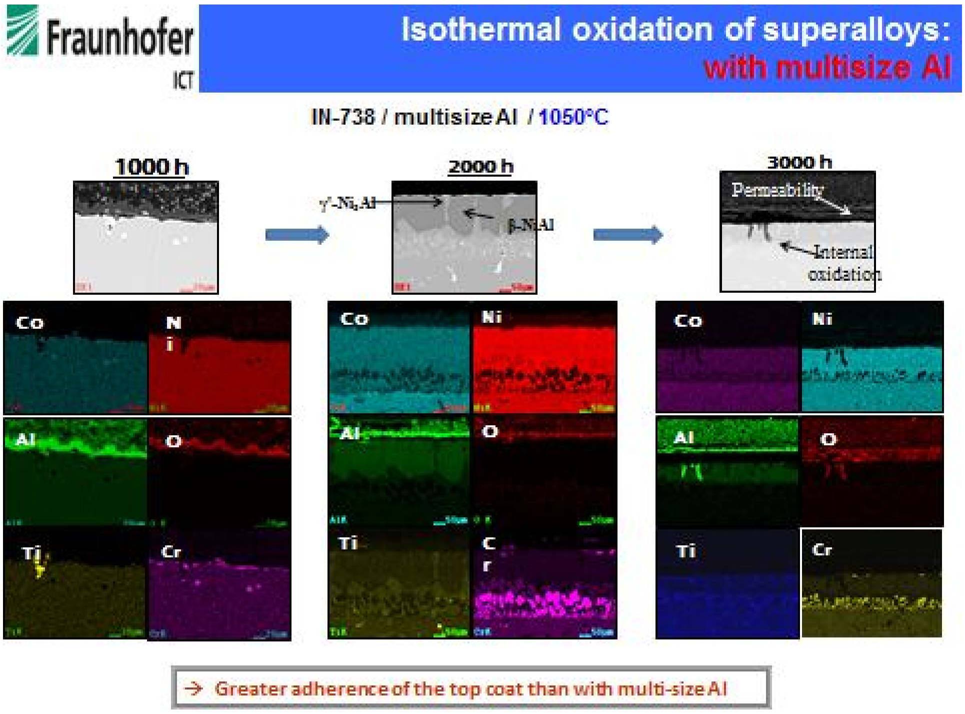
Isothermal oxidation





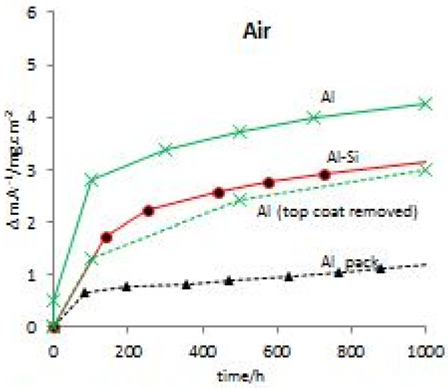
Graded structures

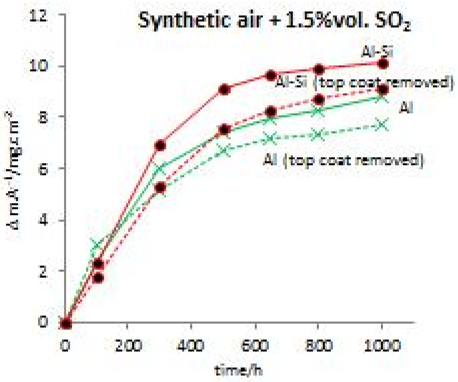




Isothermal oxidation of superalloys: Exposure at 1000° C in air and SO_2 containing synth. air

DECHEMA Karl-Winnacker-Institut



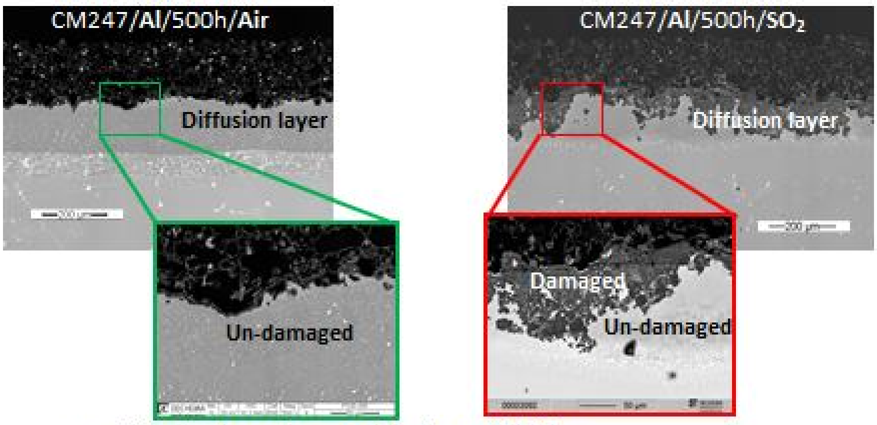


- Pack aluminization show lowest weight gain
- Al-Si coatings lower weight gain than Al coatings
- Coatings without top coat lower weight gain (top coat oxidation)

- Exposure in SO_2 increases weight gain
- Coatings without top coat lower weight gain
- Al coatings lower weight gain than Al-Si coatings (after 300 hours)

Isothermal oxidation of superalloys: Characterization after exposure in SO_2 at 1000° C

DECHEMA Karl-Winnacker-Institut



- Diffusion layer damaged due to sulfidation
- Need to quantify the diffusion layer affected by sulfidation
- Need to quantify the sulfidation depth in diffusion layer

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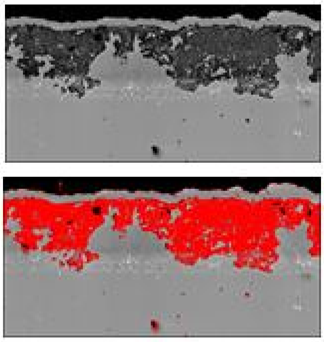
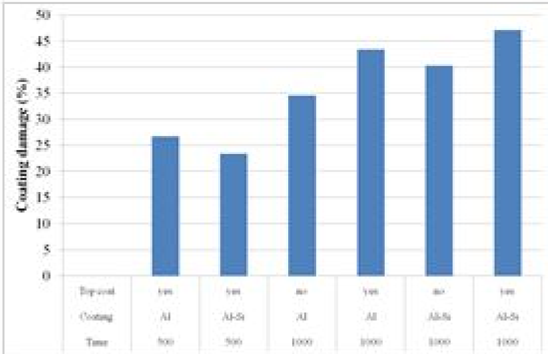
Isothermal oxidation of superalloys: Sulfidation: Remaining coating quantification



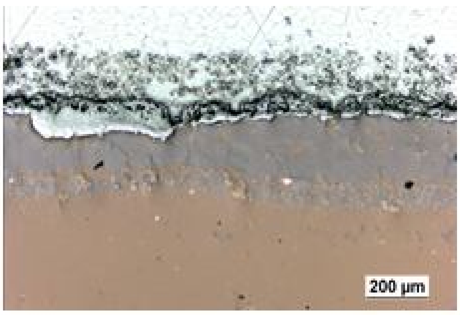


- Quantification carried out by image analysis of 175 SEM cross-sections
- Coatings without top coat show less sulfidation of diffusion layer
- Coatings of Al-Si are less protective than coatings of Al after 500 hours of exposure

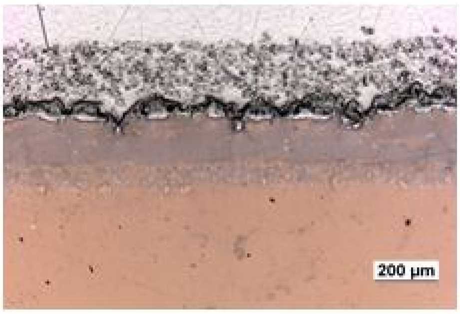
DECHEMA Karl-Winnacker-Institut

Isothermal oxidation of superalloys: Al and Al-Si in air + 340 ppm SO_2 +16 bar

CM247/**Multiple Al**/1050°C/2000h

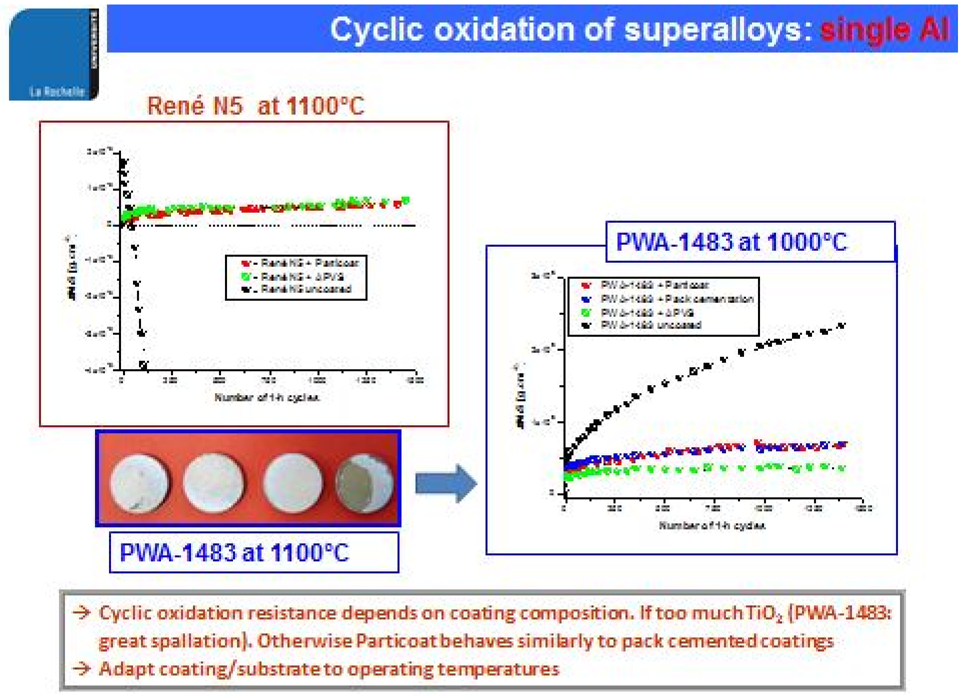


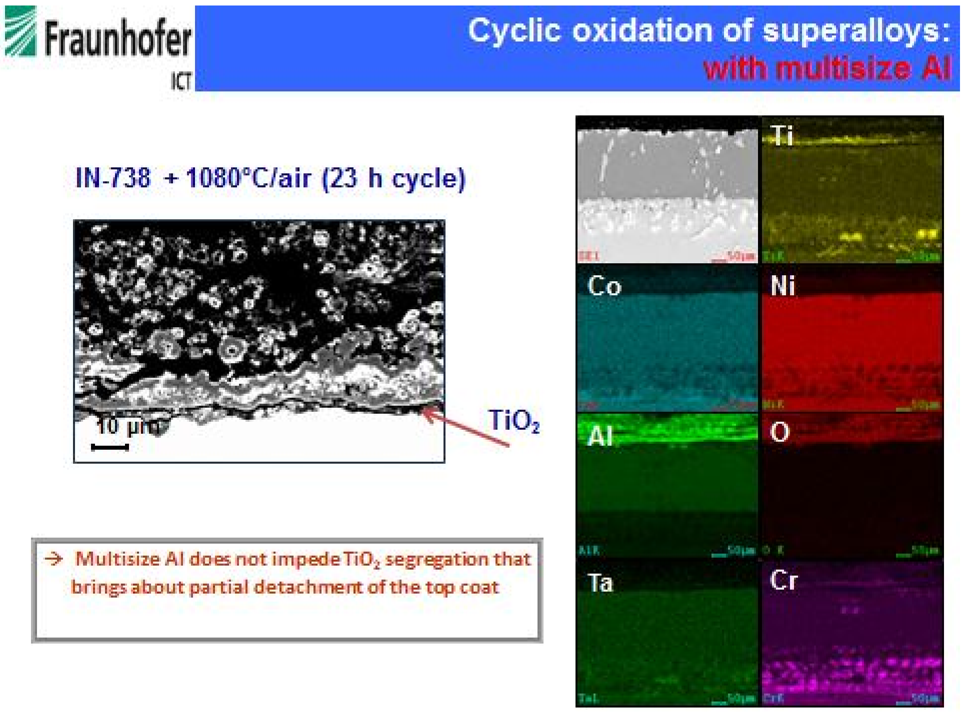
CM247/**Multiple Al-Si**/1050°C/2000h

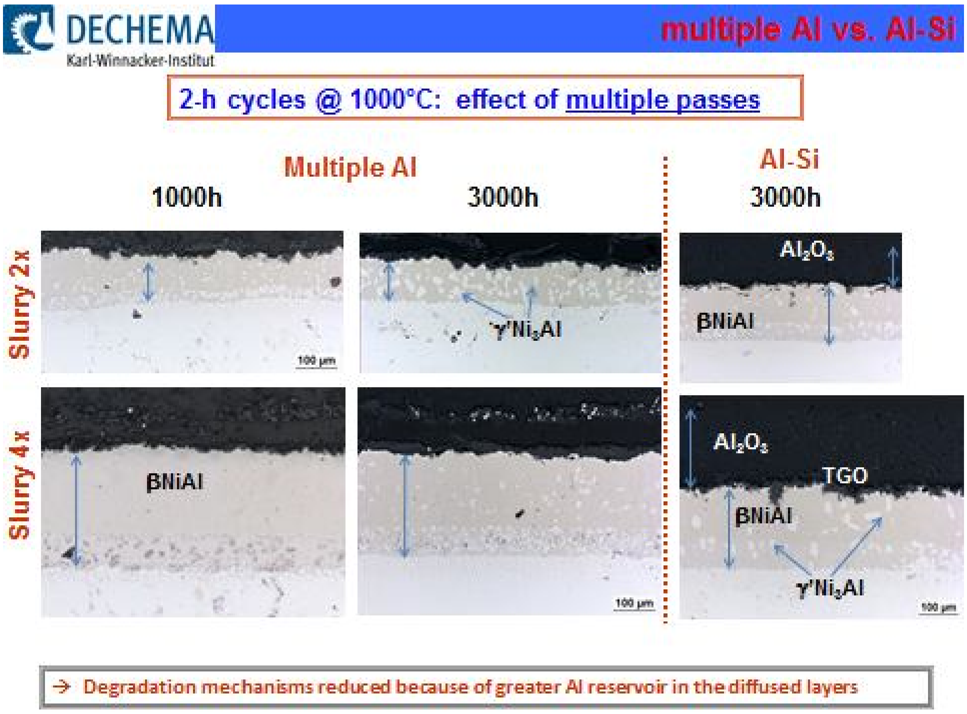


→ Top coat adherent even under high pressure
→ Local attack in Al-based slurries but no attack of the susbtrate
→ Particoat should resist in hot corrosive environments too

Cyclic oxidation

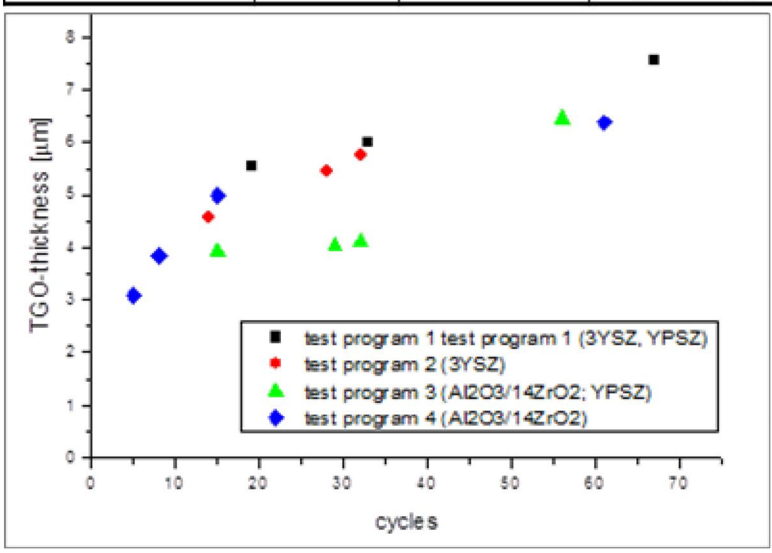




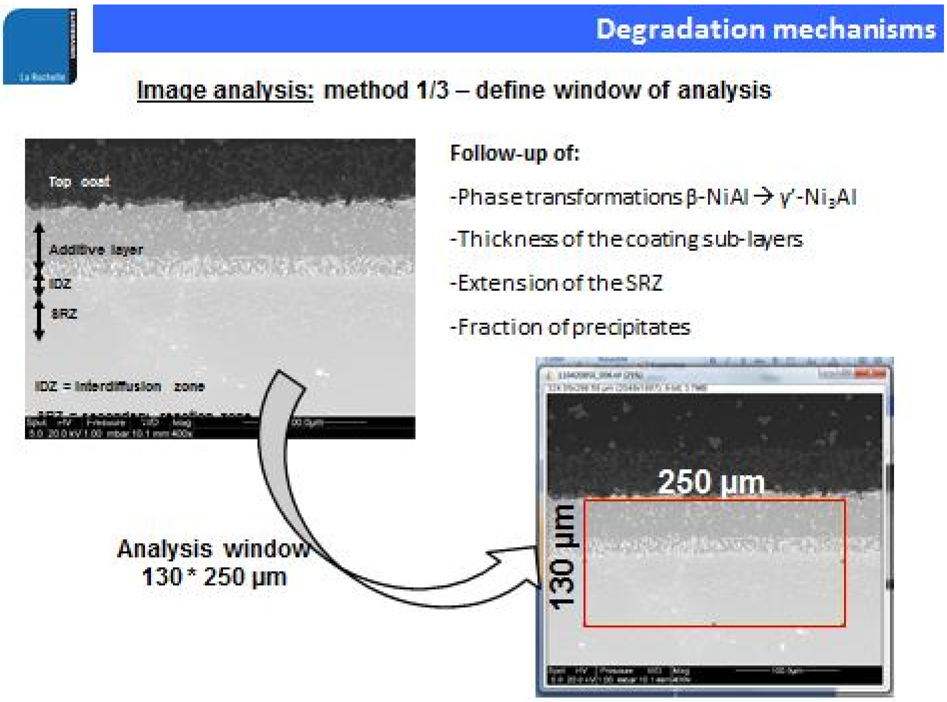


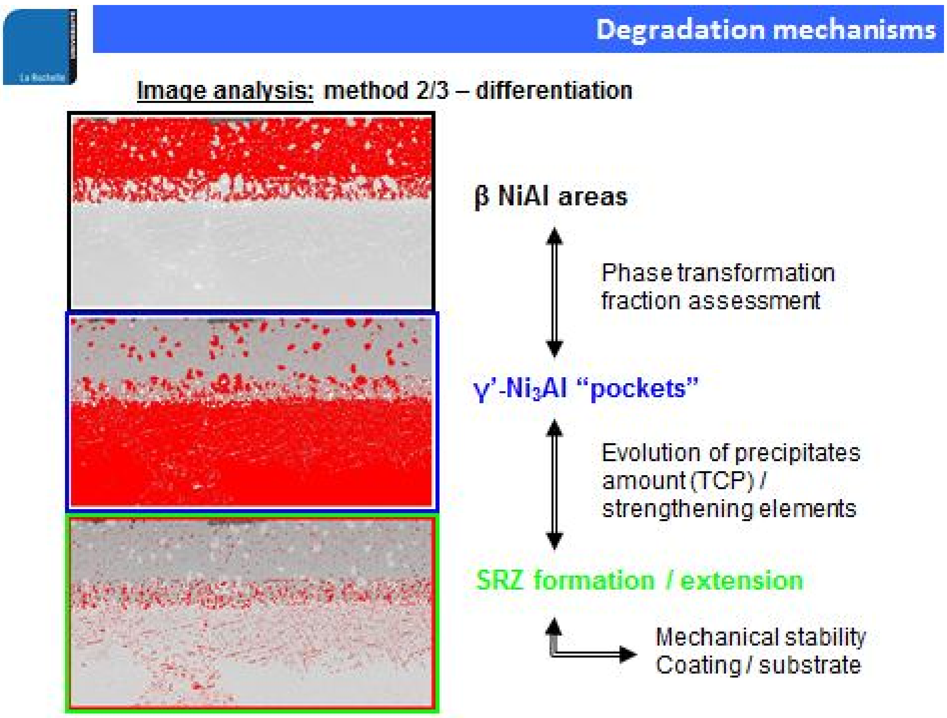
Fraunhofer ICT: Cyclic oxidation of superalloys with special design coatings

Test program	Substrate	Bond coat [180-250 µm]	1. layer	2. layer	Lifetime (cycles x 23h)
Reference sample (Siemens)	IN738LC	SC2464	YSZ		41.5 cycles
1	IN738LC	SC2464	3YSZ [90-110 µm]	YPSZ [500 µm]	67 cycles
2	IN738LC	SC2464	3YSZ [560-660 µm]	---	56 cycles
3	IN738LC	SC2464	Al2O3/14ZrO2 [240-270 µm]	YPSZ [310-330 µm]	58 cycles
4	IN738LC	SC2464	AL2O3/14ZrO2 [460-550 µm]	---	19 cycles
5	IN738LC	SC2464	YPSZ [530-550 µm]	---	80 cycles



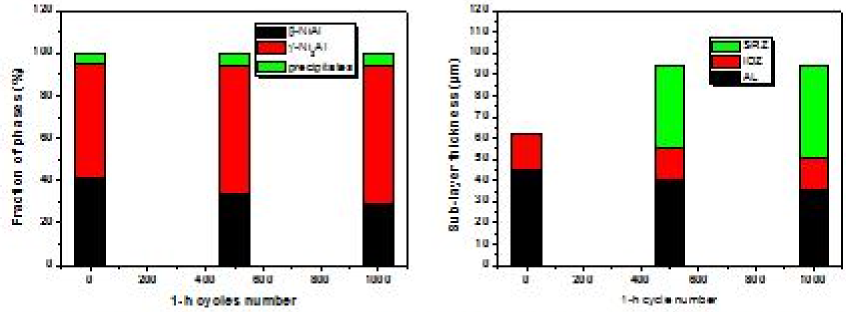
Degradation mechanisms





Degradation mechanisms

Image analysis: method 3/3 – measurements onto N5 PARTICOAT



→β-NiAl fraction decrease due to phase transformation onset (β-NiAl → γ'-Ni_3Al) by Al depletion (oxidation/interdiffusion). Slight increase of precipitates amount

→slight decrease of the AL/IDZ thicknesses after 1000 cycles @ 1100°C due to phase transformation and associated volume contraction

→development and quick increase of the SRZ extension during the first 500 cycles followed by a slow down

Conclusions:

1.- Single or multiple, mixed or unmixed Al Particoat coatings show excellent oxidation resistance with limited degradation regardless of the corrosive atmosphere (air, water vapour SO_2)
2.- Most of degradation processes occur by excessive TGO growth (strongly dependant on substrate initial composition and coating treatment) and by Al interdiffusion as in conventional coatings
3.- Pack cemented and out-of-pack coatings behave relatively worse or similar to Particoat coatings
4.-Exposure in air:

- Al-Si produced coating have shown better oxidation behavior than Al produced ones at temperatures below 1000°C

5.-Exposure in SO_2 containing atmosphere:

- Al-Si produced coating have shown excellent protection in SO_2 containing atmosphere while the Si was maintained in the diffusion layer.
- Coatings with top coat show higher weight gain than coatings without top coat probably due to a "rumpling" of the diffusion layer and to an oxygen partial pressure decrease through the top coat

Non destructive Technique selection:

- ET is the most promising technique
- UT is not able to provide reliable results due to top coat structure (hollow spheres)

Device Selection:

- Among ET devices, Salutron has demonstrated higher accuracy and robust behavior than Positector

Coating Measurements:

- NDT measurements of the top coat (hollow spheres)
- NDT techniques are not able to measure layers beneath the top coat (diffusion layers)

Nickel based alloys Measurements validation:

- Good accuracy

WP5.1.3 – Molten deposits

Interaction of the PARTICOAT coating with molten deposits

Samples

- Alloy 321 coated and heat treated
- IN 738 + Al(1-20µm)- 950°C-50h

Salt

- 40% Na_2SO_4 - 60% V_2O_5

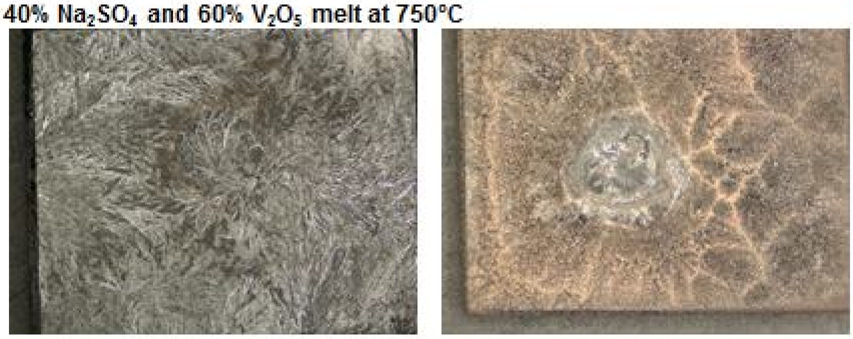
Conditions

- Atmosphere-Air
- heating rate 10 °C/min
- from RT to 675 °C (temperature thermocouple).

Furnace

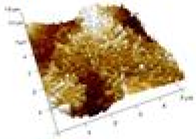
Interaction of the PARTICOAT coating with molten deposits

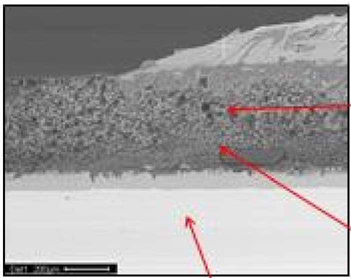
40% Na_2SO_4 and 60% V_2O_5 melt at 750°C



→ Uncoated (left) and Particoated (right) PWA-1483
→ Attack of the substrate by the melt but very localised attack in the presence of Particoat: beneficial effect but not real lotus effect

EDX- Cross Section Alloy 321 after heating with a drop of molten salt



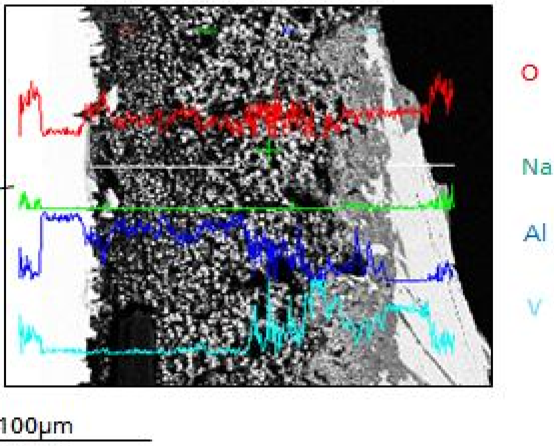


Element	Wt%	At%
OK	14.16	22.17
NaK	00.27	00.29
AlK	81.22	75.40
VK	04.36	02.14
Matrix	Correction	ZAF

Element	Wt%	At%
OK	34.75	51.85
NaK	01.52	01.58
AlK	40.14	35.52
VK	23.59	11.06
Matrix	Correction	ZAF

Element	Wt%	At%
OK	20.20	29.92
AlK	79.80	70.08
Matrix	Correction	ZAF

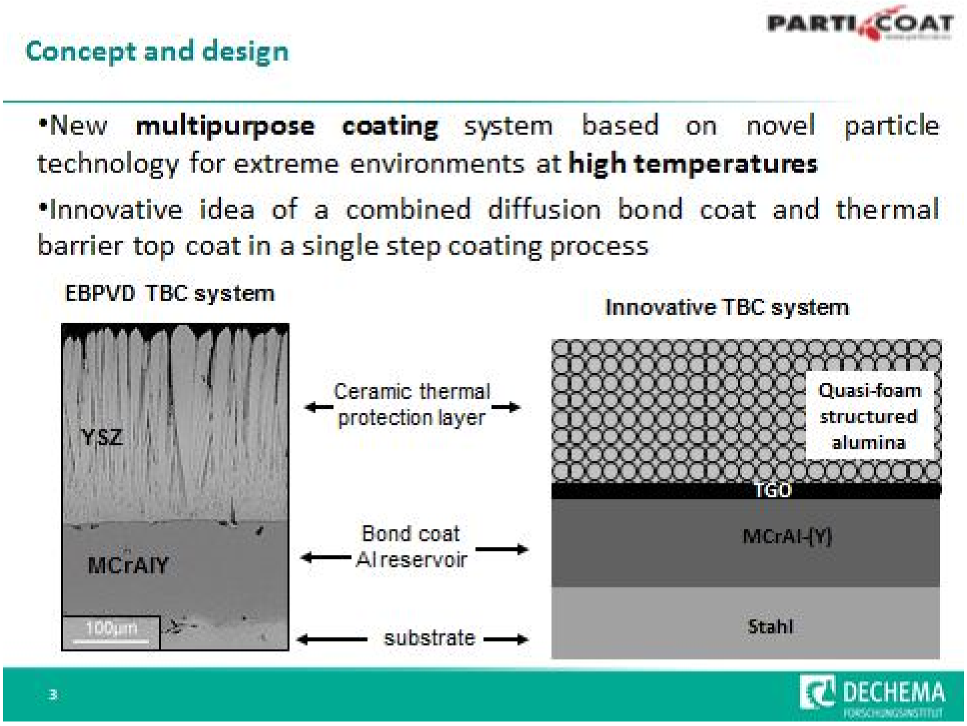
Linescan- Cross Section Alloy 321 after heating with a drop of molten salt



- PARTICOAT reacts with V and prevents its penetration to the metal surface
- Lotus effect not observed , molten deposit infiltrates the topcoat

WP5.2 – Mechanical properties

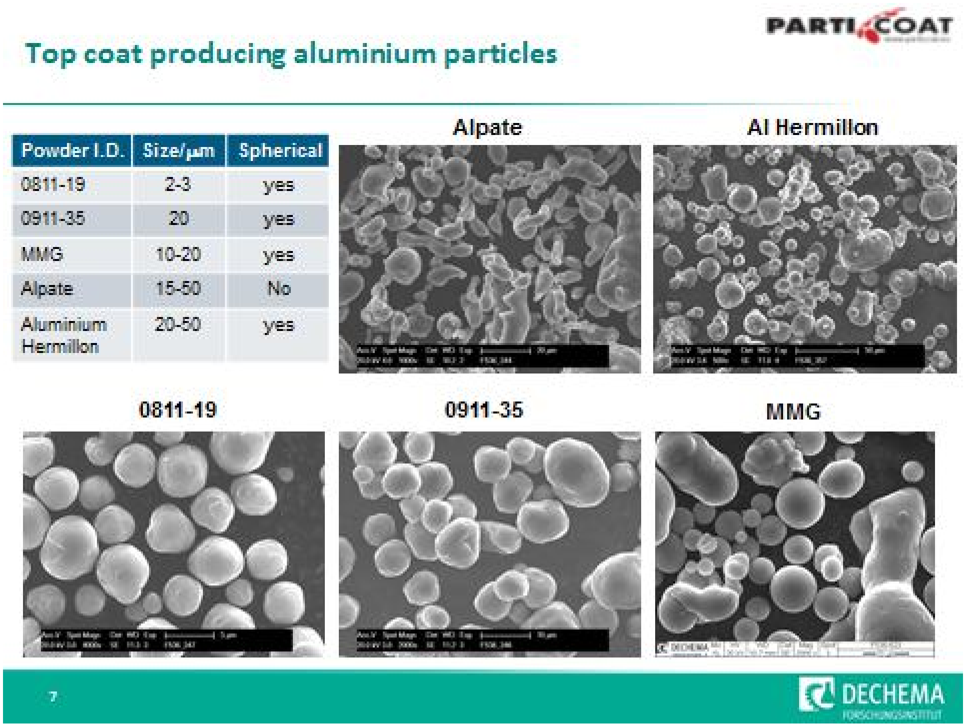
Introduction



Lifetime of thermal barrier coatings:

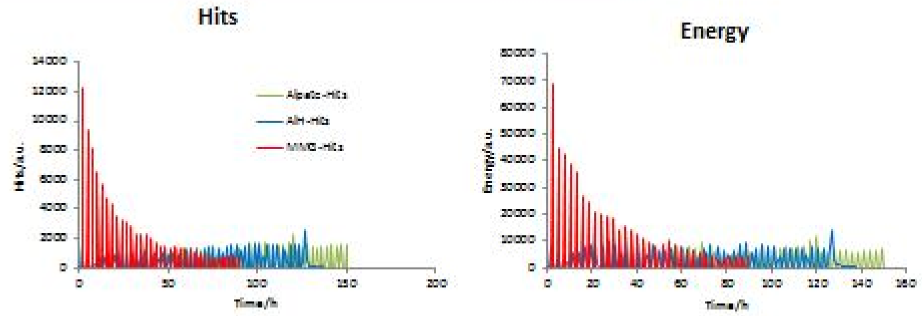
1. Thermal fatigue
   - Coefficient of thermal expansion (CTE)
2. Thermal ageing
   - Thermally grown oxide (TGO)
   - Sintering
3. Bond coat depletion of aluminium

Particle size influence on adherence



Powder I.D.	Size/µm	Spherical
0811-19	2-3	yes
0911-35	20	yes
MMG	10-20	yes
Alpate	15-50	No
Aluminium Hermillon	20-50	yes

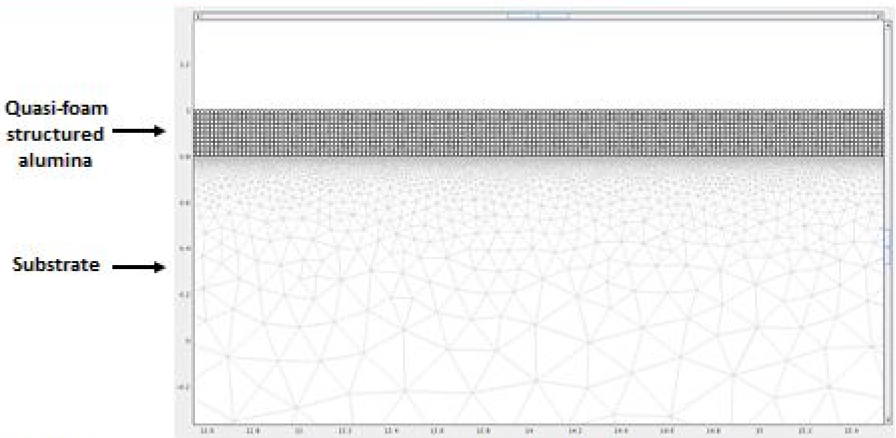
Thermal ageing by cyclic exposure at 1100°C



- 0911-35 showed spallation since the beginning of the test
- MMG has shown large crack propagation
- Alpate and Hermillon show similar crack propagation. These coatings were adherent after 300 hours exposure.

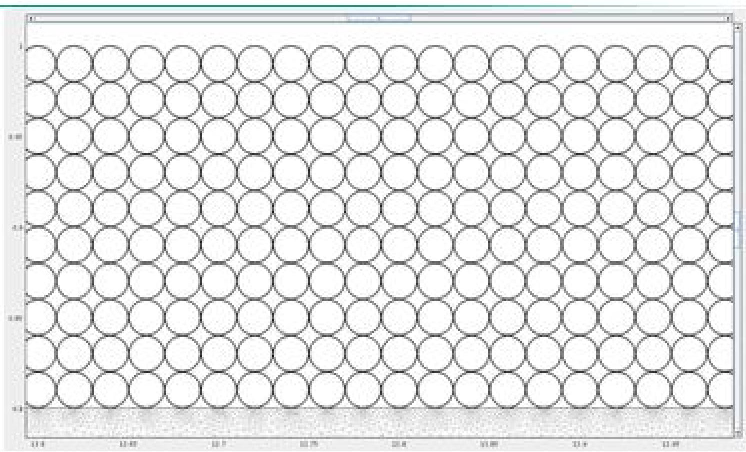
Modeling of particle size effect under pressure

System designs and meshing (I)



- Simulation of a top coat based on spherical hollow particles in direct contact with the metallic substrate

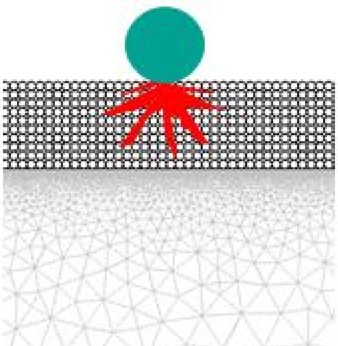
System design and meshing (II)

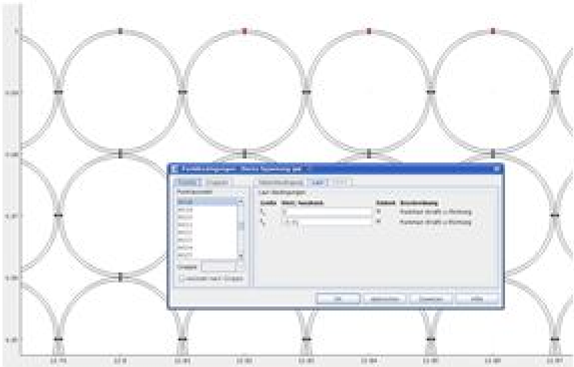


- Top coat thickness of 200 µm
- Spherical particles with 20 µm diameter

Definition of material and boundary conditions

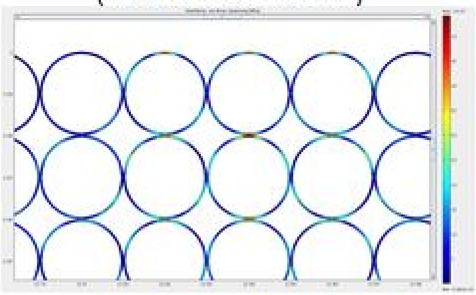
- Simulation of the 4-point bending experiment
- Effect of a cylinder pressure on the top coat



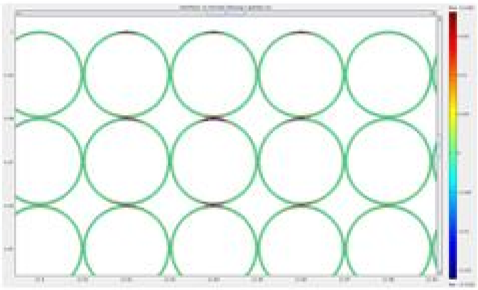


Modeling results

Stress distribution in particles (Von Mises criterion)

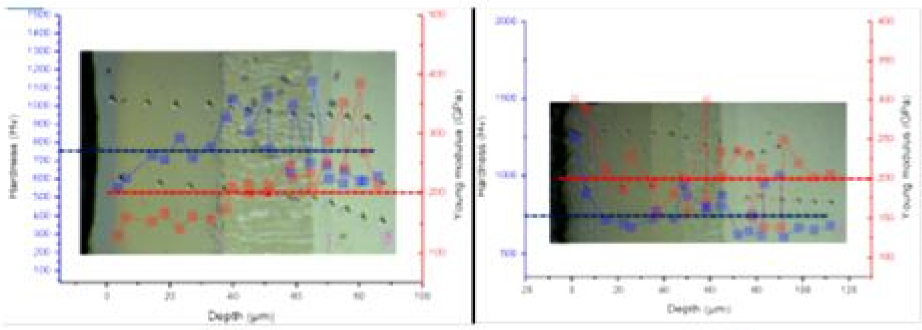


Strain in X direction



- 100 mN locally applied
- Main stress and strain localized on top of oxide shells
- 80 mm coating affected in deep by applied pressure
- 60 mm coating affected in width by applied pressure

Hardness of the diffusionzone



(a) (b)

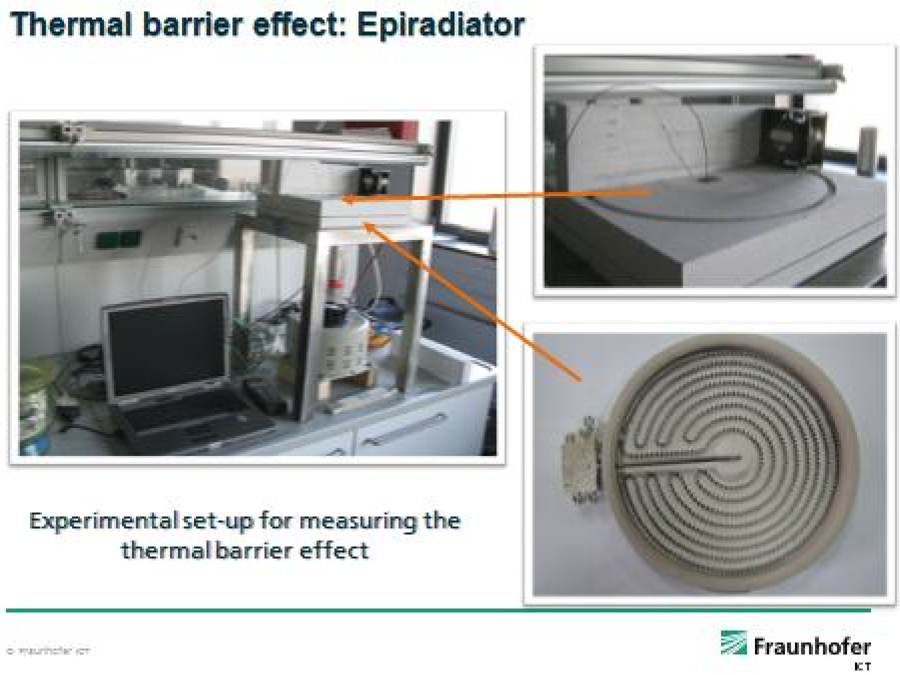
Vickers nano-hardness profiles and the corresponding Young's modulus of the different areas of the coating after full heat treatment of (a) Particoat and for (b) the conventional APVS coatings.

<u>Conclusions</u>

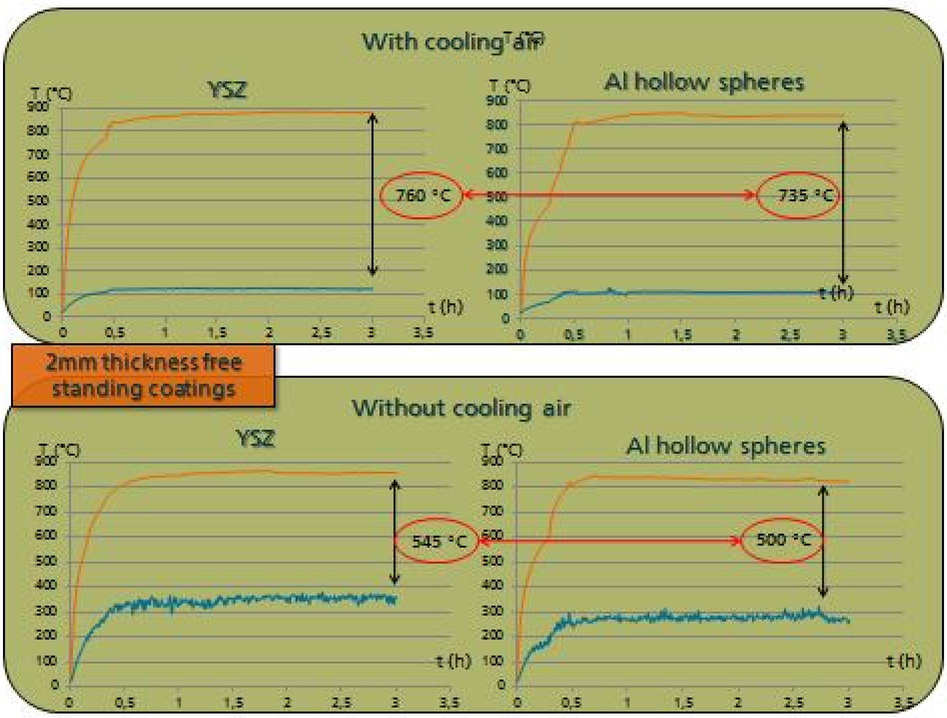
- 4PB coupled to AE does not provide adequate information for the PARTICOAT coatings case
- Cyclic oxidation coupled to AE test has shown that aluminium particles must have a minimal diameter of 20 mm in order to produce an adherent top coat
- Simulation of stresses on top coat has demonstrate that the substrate will not be affected by pressure directly applied on top coat
- Top coat is prone to erosion because of the high porosity and structure, but the diffusion zone can withstand high abrasive loads

WP5.3 – Thermal barrier effect

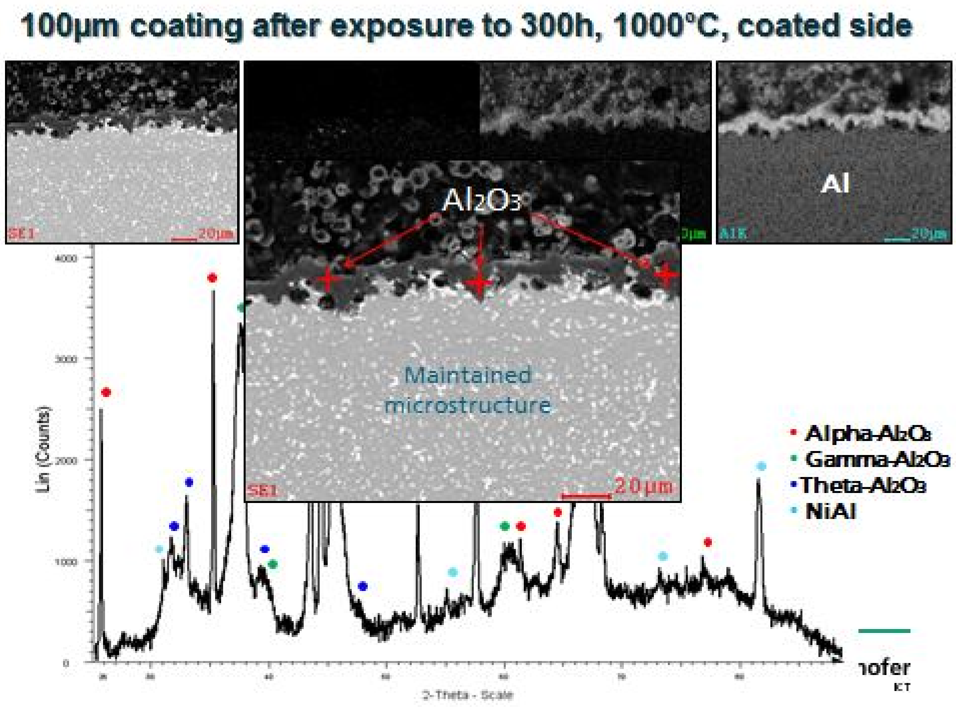
Experimental set-up with heat insulation in the surroundings of the sample and possibility of cooling the sample back side:



Comparison of the thermal barrier effect of PARTICOAT to a conventional TBC from YSZ:



Effect of the thermal barrier of PARTICOAT on the oxidation of the substrate when exposing the coated side to 1000°C and cooling the back side:



The presence of the metastable alumina phases γ- and θ-Al_2O_3 indicates a temperature gradient within the topcoat and temperatures below 650°C at the interface to the diffusion zone.

Conclusions:

- Particoat shows a pronounced thermal barrier effect, which is comparable to the conventional YSZ - TBC.
- It's confirmed that due to the TBC effect, the base metal will be protected, the temperature at the metal surface is notably reduced.

WP5.4 – In field testing

<u>SVUM</u>

PARTICOAT layer preparation

- 347 H (cuts of a tube – 20 x 10 x 5 mm)
- Surface only mechanically filed by and degreased in acetone
- Al micropowder 3 – 5 µm

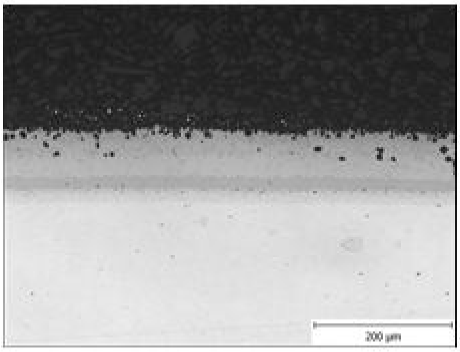
PVA based slurry (50 % Al, 1 % PVA, 49 % H_2O)

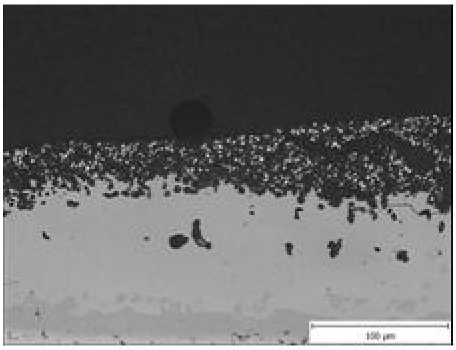
Deposition by dipping,
thickness of the layer approx. 200 – 300 µm

Annealing at 800 °C for 8 h (heated in air)

Lanzarotte 2012

PARTICOAT layer preparation





- High quality compact coating at 347 H, over 100 µm thick
- Three layer structure, outer layer is growing by outward iron diffusion
- Partially oxidized Al particles (a top coat)

Lanzarotte 2012

PARTICOAT vs. Hot dip aluminizing

• PARTICOAT technology

- slurry: PVA based, Al particles 3 – 5 µm
- painting: 200 – 300 µm thick layer
- annealing: 800 °C/8 h, air

- applied only to austenitic steel
- easy and cheap application

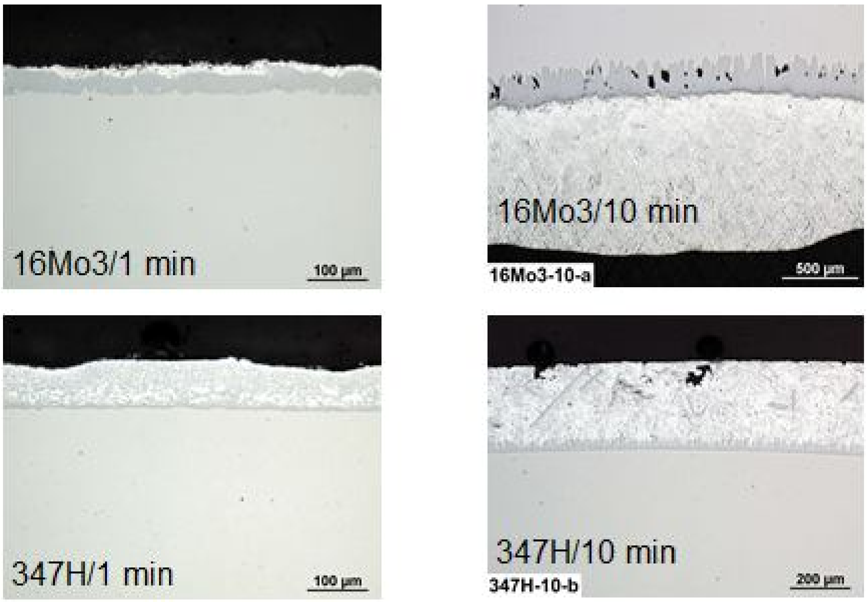
• Hot dip aluminizing (HDA)

- dipping into molten aluminium bath
- under NaCl/KCl/NaF flux
- 800 °C/1 min

- very fast process
- ferritic 16Mo3 is possible to coat
- more difficult application

Lanzarotte 2012

800 °C, aluminium bath



Field tests (WIP Prague)

- **Exposition started in April 2011**
- **Corrosion rings situated in a boiler, average temperatures 540, 610, 660 °C, exposure time 4820 h**

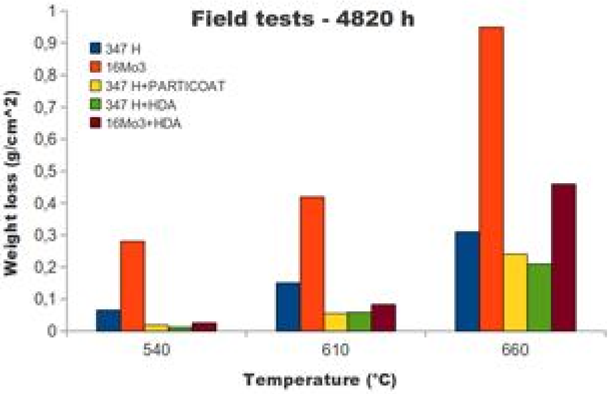
Situation after exposition

- Large amount of salt deposit with high amount of chlorine
- Before evaluation the deposit was removed by stream of water

Composition of fly ash (wt. %)										
Na	Al	Si	S	Cl	K	Ca	Ti	Fe	Zn	Pb
1.80	1.60	1.65	1.30	3.90	0.36	7.80	0.30	0.61	1.20	0.57

Field tests – results

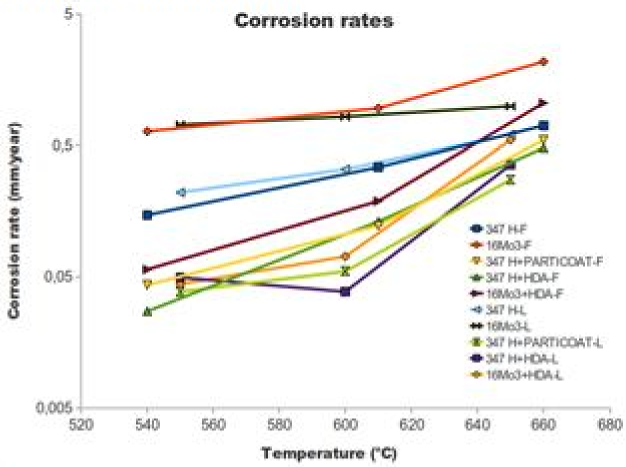
- Weight losses evaluated
- All coatings indicate similar corrosion properties
- Corrosion rates below 600 °C are near 0.05 mm/year



Lanzarotte 2012

Field tests – results

- Calculation of corrosion rates – linear fit of expeimental results
- Comparison of field and laboratory tests under deposit
- Field conditions are more harmful



Lanzarotte 2012

Conclusions

- Corrosion resistance of candidate coatings is very good below 600 °C. Estimated corrosion rate is 0.05 mm/year in field conditions.
- PARTICOAT exhibits excellent resistance in HCl/SO_2 containing gases Aluminium depletion simulated – not critical for lifetime – corrosion is dominant degradation mechanism.
- Typical lifetime of austenitic superheaters at 500 °C in waste/biomass plants is 3 years. According to the our calculations PARTICOAT lifetime under this conditions is at least 2 years. Price of the new superheater is about
- 400 000 EUR, this means about 50 000 EUR cost savings per year.

TECNATOM

- WP5.4 objectives:
  - To carry out “in-field” testing for selected applications in order to understand the degradation mechanisms and verify the performance under real conditions.
- In particular:
  - To perform “in-field” testing in a fossil power plant boiler.
  - Coating samples have been inserted in the LOCA test facility located at TECNATOM headquarters.

LOCA CHAMBER DESCRIPTION

- Facility oriented to reproduce nuclear reactor situations and also to investigate the effect of several degradation mechanisms such as oxidation and corrosion.
- It has an adequate data acquisition system to continuously monitor and record the test outline.

- Max. Temp.: 250ºC
- Max. Pressure: 10 bar
- Test volume: 1m³

PARTICOAT tecnatom

SAMPLES LOCATION

- Samples were located horizontally inside the LOCA boiler, just close to the exhaust gas outlet.

PARTICOAT tecnatom

Test conditions

- **Date**: July 18th-19th, 2012
- **Test duration**: 30 hours at nominal pressure and temperature.
- **Location**: Burner exhaust gas outlet.
- **Temperatures**: 420ºC-480ºC

THICKNESS MEASUREMENT

- **Eddy-current portable devices:** Positector & Salutron
  - After and before boiler test
- **SEM validation**

	Before boiler test		After boiler test		SEM Measurements
	Positector	Salutron	Positector	Salutron	
SAMPLES	THICKNESS (µm)	THICKNESS (µm)	THICKNESS (µm)	THICKNESS (µm)	THICKNESS (µm)
SS321 (#2C)	168	157,8	138	142	115
IN738 (#3C)	102	100	108	101	100
P91-4L (#C)	216,4	238	208,2	239,5	200
AISI347-2L (#C)	1571,9[*]	454,6	1563,3[*]	447,1	90
AISI347-3L (#C)	1716,3[*]	521,8	1660,5[*]	491,3	100
AISI347-4L (#C)	1955,7[*]	560,8	1885,3[*]	550,6	115
40DSA-650 (#1C)	101,9	94,8	87,3	83,7	50
40DSO (#C)	848	1033,6	880,3	1081,9	650

Conclusions

- **In field testing**:
  - Nickel based alloy: very good performance
  - Ferritic steel: good performance
  - Stainless steel: medium performance
- **NDT accuracy**:
  - Nickel based alloy: very good accuracy
  - Ferritic steel: good accuracy
  - Stainless steel: bad accuracy

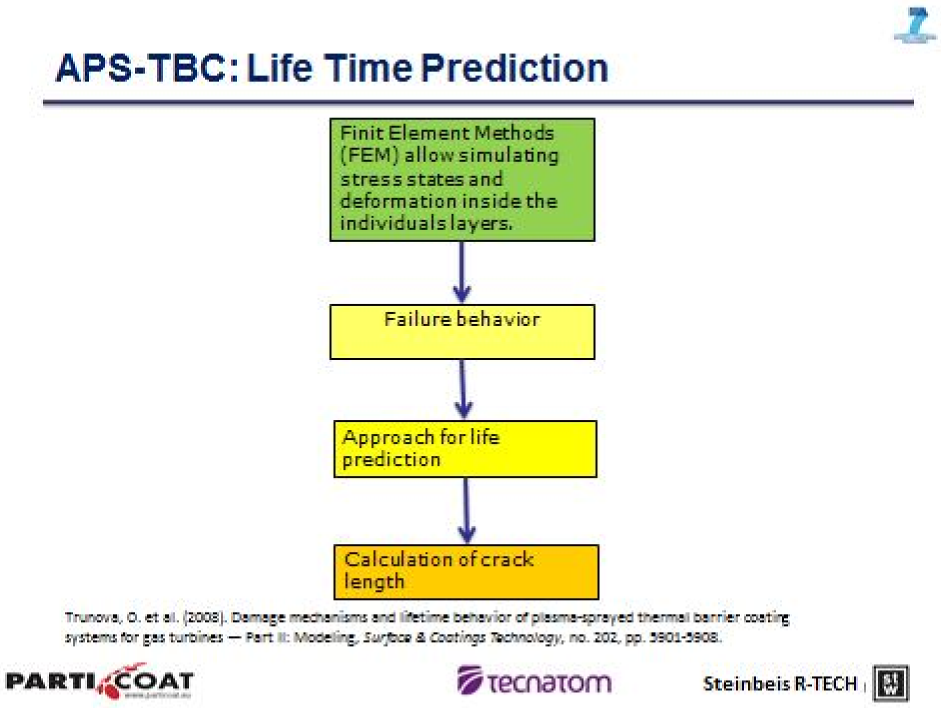
WP5.5 - Modelling

- WP5.5 overall objectives:
  - To obtain mathematical models of degradation mechanisms
  - Long term progress for estimating the lifetime as a function of:
    - Coating system
    - Temperature
    - Coating thickness
- In particular:
  - To perform modeling with data from non-destructive inspection methods for understanding of the degradation mechanisms.

Methodology

- Main degradation mechanisms to be considered:
  - Thermal fatigue
  - Thermal ageing, basically associated to thermally grown oxide (TGO)
  - Bond coat depletion of aluminum
- Analysis of experiments carried out by Particoat partners

➔ To provide coating evolution models.



APS-TBC: Life Time Prediction

Finit Element Methods (FEM) allow simulating stress states and deformation inside the individuals layers.

Failure behavior

Approach for life prediction

Incubation phase

Ends when *dtgo* reaches approx. ¼ of the averaged peak-to-peak roughness of the bond coat Rz.

Propagation phase

Fracture mechanics approach:

The stresses induced by thermal mismatch, and stresses induced by TGO growth is applied for the calculation of **macrocrack** propagation.

APS-TBC: Life Time Prediction

Finit Element Methods (FEM) allow simulating stress states and deformation inside the individuals layers.

Failure behavior

Approach for life prediction

Calculation of crack length

Incubation phase

- The crack length is assumed to grow linearly with TGO until TGO thickness of ¼ Rz (BC) is reached
- Max crack length at the end of the incubation phase = ½ of wavelength of the roughness profile of the bond coat

Propagation phase

Energy release **G** have two major sources

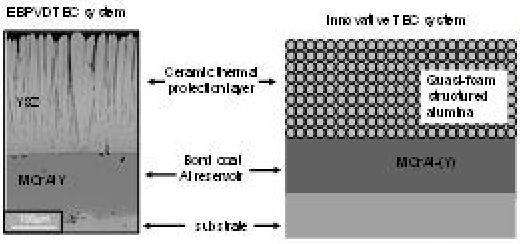
G EI: Impact of thermal mismatch (elastic behavior) - Delamination

G TGO: Reflects the contribution by lateral growth of TGO

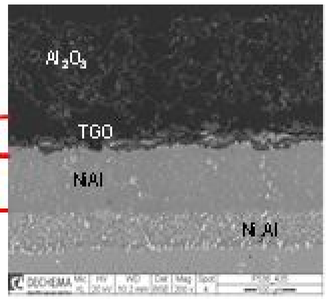
Trunova, O. et al. (2008). Damage mechanisms and lifetime behavior of plasma-sprayed thermal barrier coating systems for gas turbines — Part II: Modeling, *Surface & Coatings Technology*, no. 202, pp. 5901-5908.

PARTI COAT www.particoat.eu tecnatom Steinbeis R-TECH

PARTICOAT: Life Time Prediction



So far the general applicability of life time criteria for TBCs.

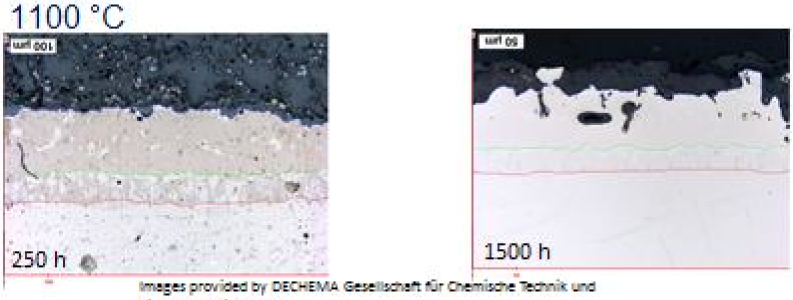


Critical TGO Thickness?

Critical Area Bond Coat?

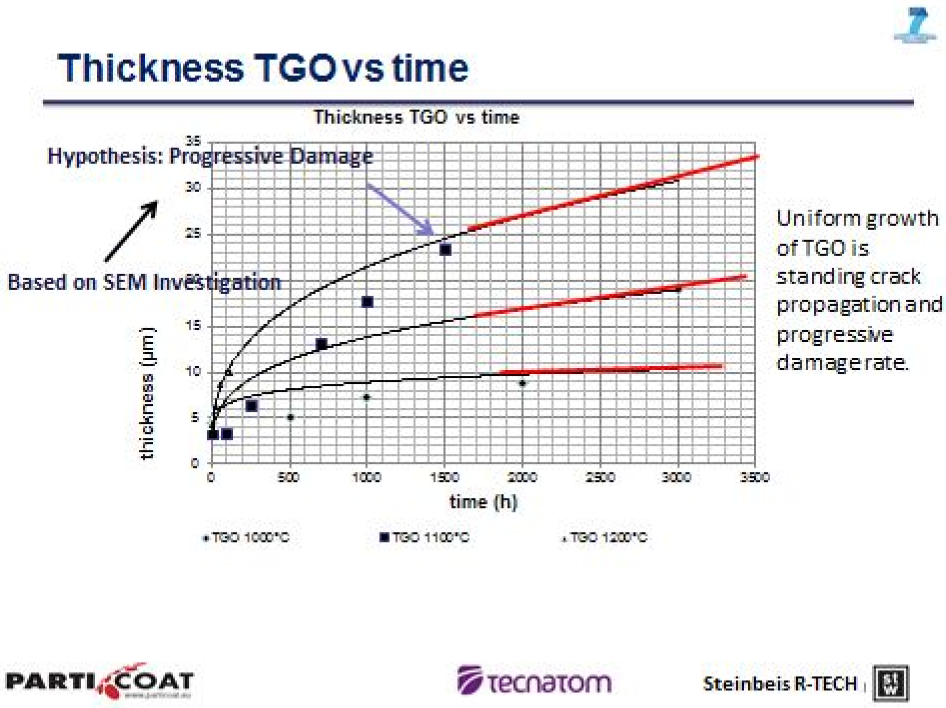
PARTICOAT : Analysis of micrographs and TGO thickness measurements

- 1100 °C



Images provided by DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e. V.

- At 250 h depletion of aluminum is observed in the diffusion zone as well as the formation of the interdiffusion zone.
- At 1500 h it is observed the large growth of the TGO layer.

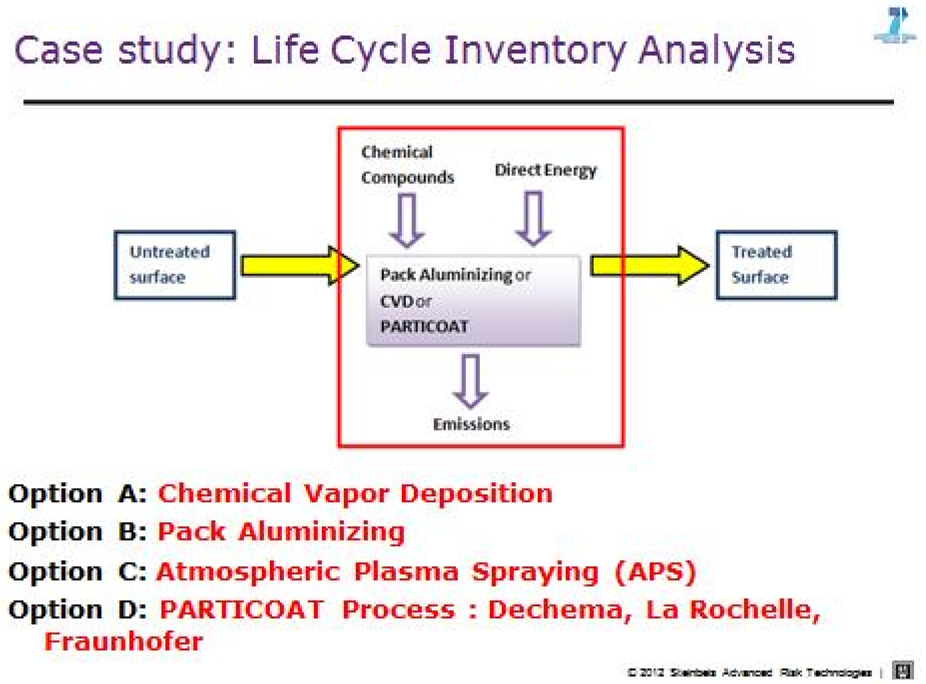


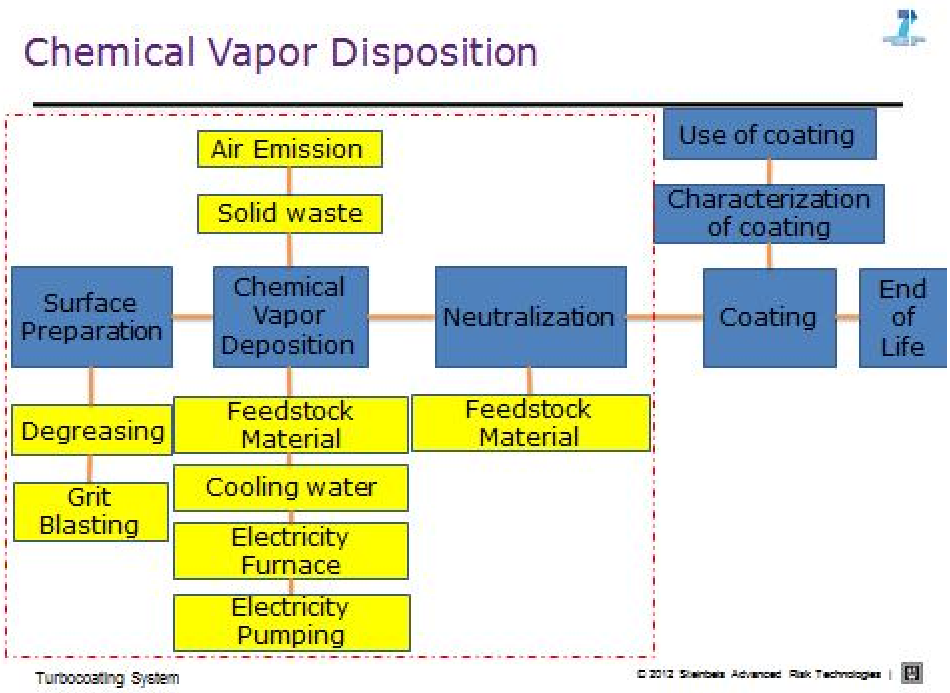
Conclusions

- PARTICOAT coating life time is limited by aluminum reservoir depletion.
- Similarities in damage development in APS TBC and PARTICOAT Coating have been used for assessing risk and uncertainty.
- TGO growth data forms a basis for assessing risks and uncertainty.
- It could be demonstrated through uncertainty analysis the high scattering of the current data.
- Further experimentation is needed in order to understand the failure behavior of the novel approach PARTICOAT especially with regard to other loading histories (eg. thermal fatigue)
- Thus experiments in mechanical properties should be further develop such as:
  - Young Modulus in the TGO and TBC
  - Calculation of stresses induced in the TBC, substrate Calculation of stresses induced in the TGO growth,
  - Lateral strains…
- When the diffusion layer is finished, existing cracks pattern grow and it appears delaminating between TGO and TBC.

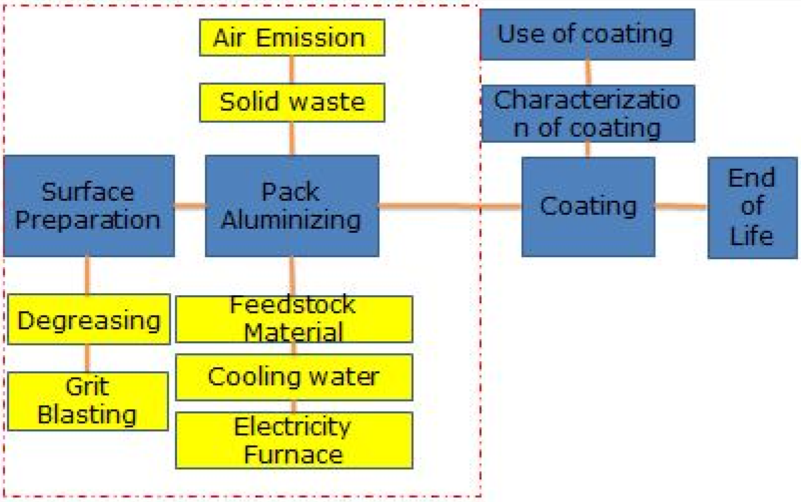
WP6 – Life cycle assessment

- This study compares PARTICOAT technology with three standard coating processes.
  - Chemical Vapor Deposition (CVD)
  - Pack Aluminizing
  - Atmospheric plasma spraying (APS)
- Functional Unit : Area of coating : approx. 300 cm^2, weight: 1 kg
- Boundaries: Gate-to-Gate Analysis
  - Process and materials used to manufacture the coating feedstock
  - The deposition process
  - Exclusion of the manufacturing of the infrastructure materials (spray guns, furnace, sprayers, …)
- Environmental comparisons were carried out using SimaPro software.



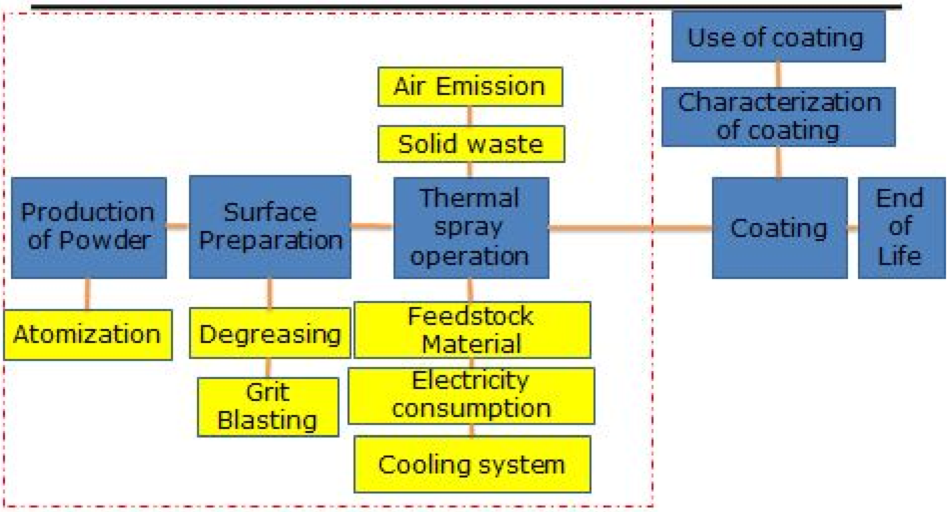


Pack Aluminizing



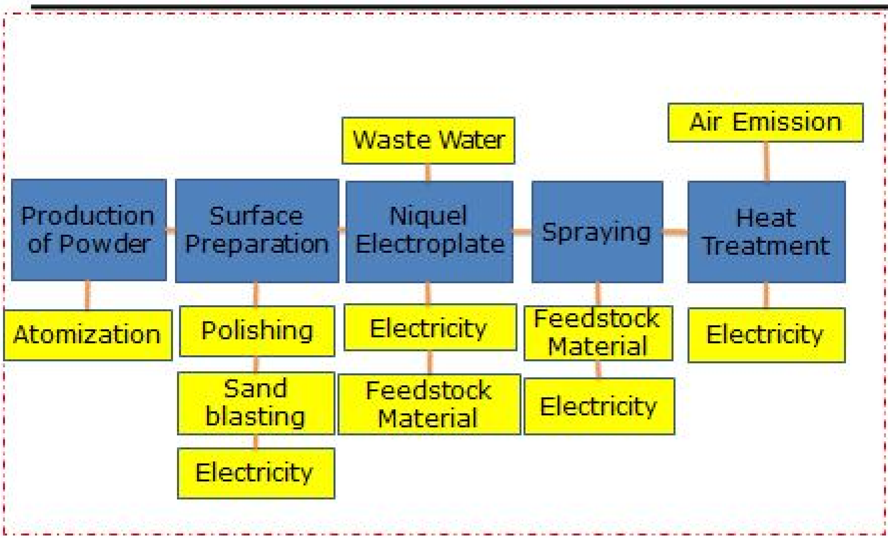
Turbocoating System

Air Plasma Spraying (APS)



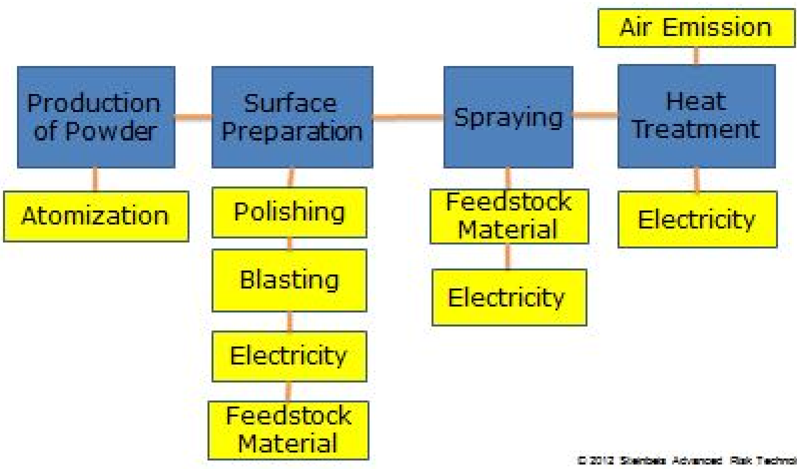
Serres, N. et al. (2009). Dry coatings and ecodesing part. 1 - Environmental performance and chemical properties. Surface & Coatings Technology no. 204, pp. 187-196

PARTICOAT Process - Dechema

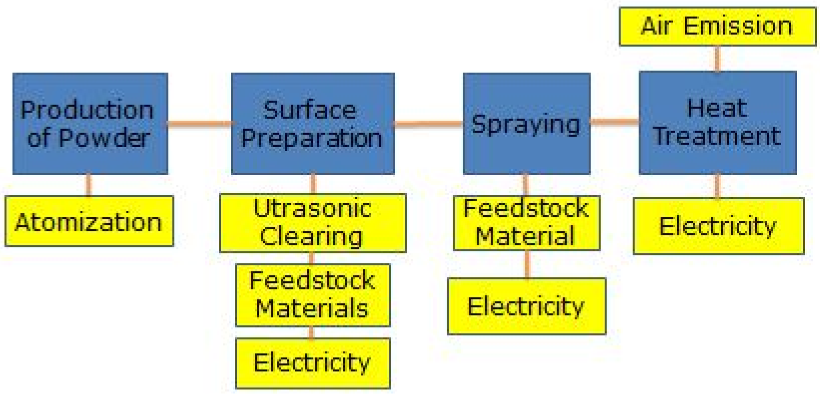


Serres, N. et al. (2009). Dry coatings and ecodesing part. 1 - Environmental performance and chemical properties. Surface & Coatings Technology no. 204, pp. 187-196

PARTICOAT – ULR



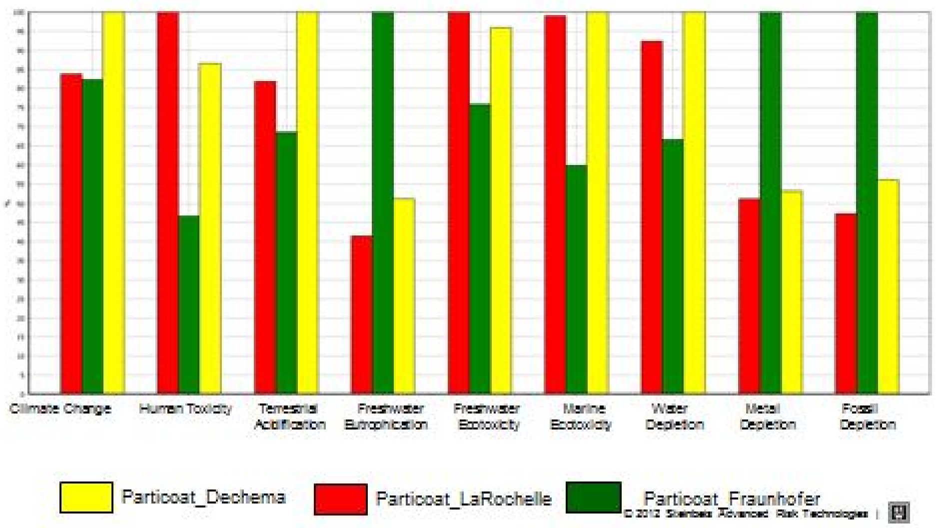
PARTICOAT – Fraunhofer ICT



Life cycle impact assessment

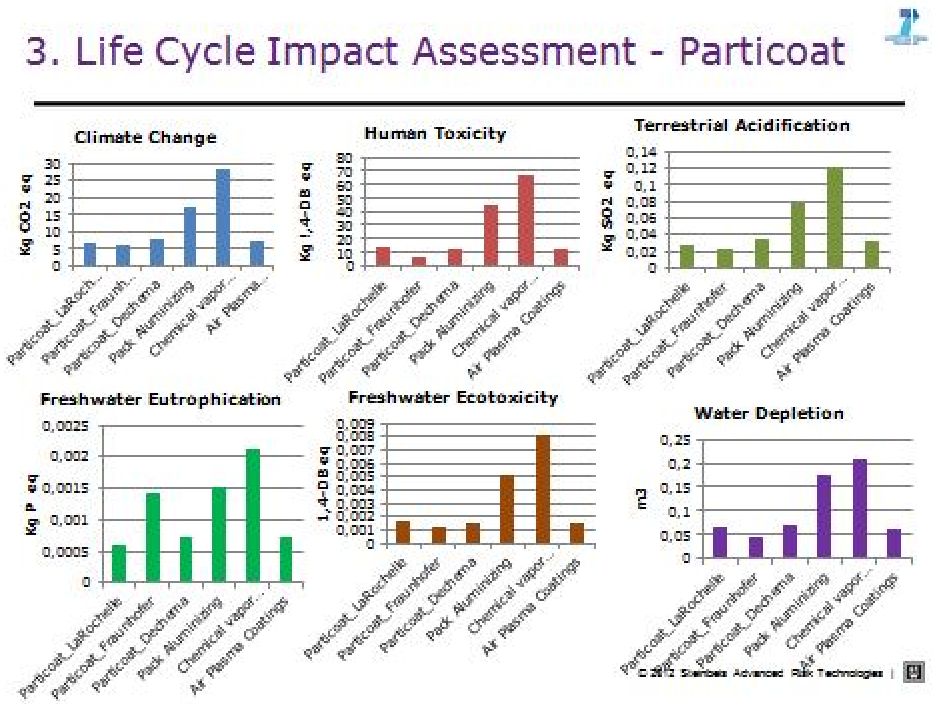
- Objective: The primary objective of the ReCiPe method is to transform a long list of Life Cycle Inventory results into the limited number of indicator scores.
- ReCiPe is a follow up of Eco-indicator 99 and CML 2002 methods. It integrates and harmonizes midpoint and endpoint approach in a consistent framework - with associated sets of characterization factors.
- List of characterization factors and documentation about the method can be found at http://www.lcia-recipe.net/
- Midpoint and endpoint characterization factors are calculated on the basis of a consistent environmental cause-effect chain, except for land-use and resources
- SimaPro LCA program and a peer-reviewed database of upstream materials and energy (EcoInvent) were used to conduct the upstream analysis of material and processes.

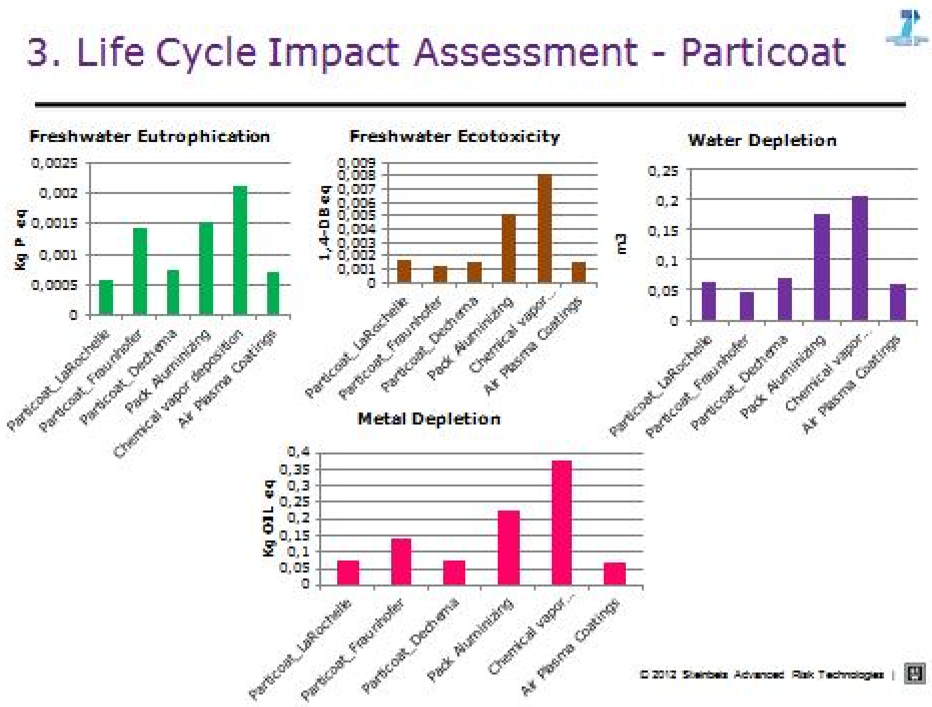
2. Life Cycle Impact Assessment – Particoat Processes



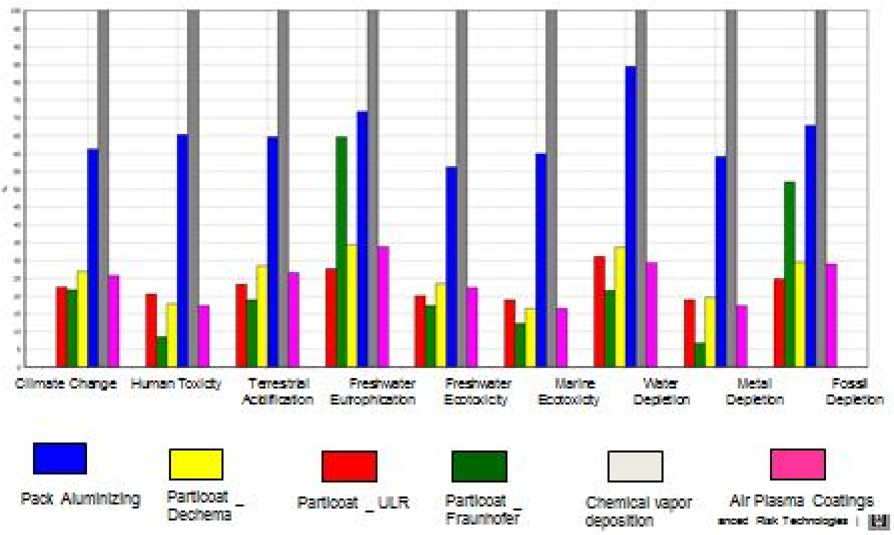
<u>Considered Factors</u>

- Climate Change: Use of Electricity
- Human Toxicity: Use of Alumina Powder in sand blasting /Use of electricity
- Terrestrial Acidification: Use of Electricity
- Freshwater Eutrophication: Fraunhofer – Production of Ethanol
- Freshwater Ecotoxicity: ULR Aluminum Oxide
- Marine Ecotoxicity: Electricity, Aluminum Oxide
- Water depletion: Use of electricity
- Metal Depletion: Fraunhofer – Use of Ethanol (from Ethylene)





3. Life Cycle Impact Assessment – Coating Processes



<u>Conclusions</u>

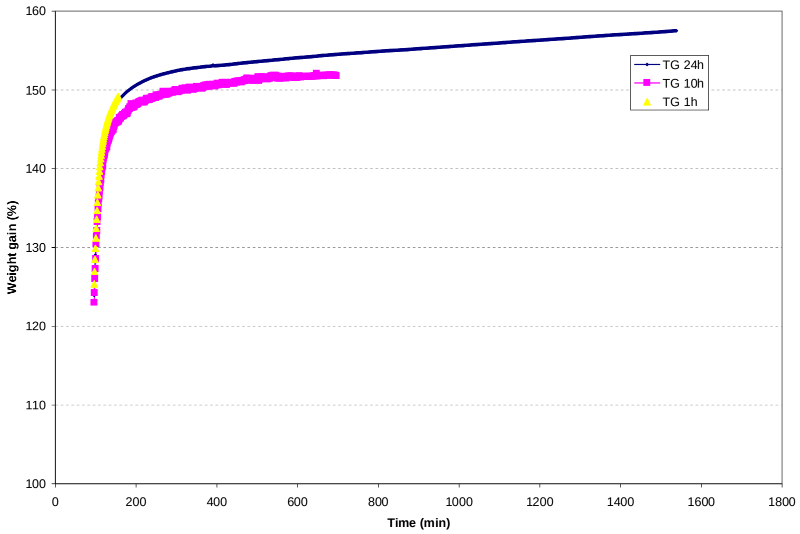
- Heat treatment is the most relevant process in the coating technologies analyzed due to the high energy requirement.
- Quantities of raw materials are small compare to the high use of energy. The amount of electricity use in the heat treatment in Particoat is responsible for about 70-80% of the environmental impacts.
- PARTICOAT produced by Dechema shows the biggest impact in the categories influenced by use of energy, however the use of ethanol in Fraunhofer process and the use of Aluminum Oxide in ULR process impact other categories.
- The APS procedure used in this study takes into account production of Zirconia powder, surface treatment and thermal spraying process and not the complete process of an APS with a VPS layer. Under this fact results are comparable with PARTICOAT meaning that a complete ASP will have much higher environmental impact.
- The high environmental impact of CVD and Pack Aluminizing is due to the use of resources, electricity: heat treatment.
- Life Cycle Assessment is a methodology which identify the potential environmental impacts associated to a product/process by using available and reviewed impact assessment methods.
- Based on the results on this study, Particoat coating shows to be a greener process (less energy and material requirements) which in one single step, bond coat and top coat layers are formed.

WP7 – Particle production for fire protection

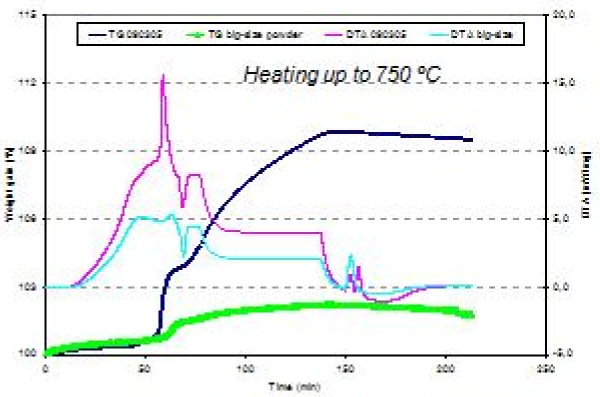
<u>TG/DTA Study of the oxidation of µm-Al particles</u>

0903-05 powder (Al 58% 0-5 µm, 38% 5-10%, 4% 10-20 µm)
Heating/cooling rates: 10 ºC/min
Air
Temperature / time: 750°C - 850°C - 950ºC ; 1-10-24 h
Temperature / time: 1050°C – 1150°C - 1250ºC ; 10 h
0903-05, 09030-4, commercial atomized powders
Temperature / time: 750 ºC ; 1 h

<u>Reproducibility:</u>



HEATING PEAKS' ANALYSIS: COMPARISON WITH BIG-SIZE POWDERS



Big-Size Powder

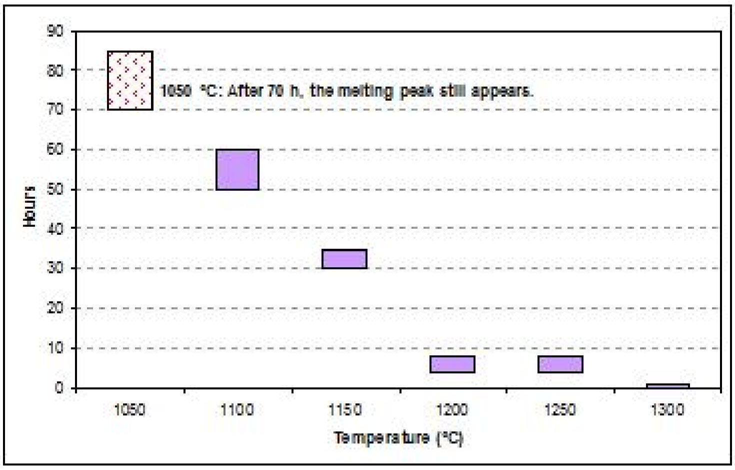
10%: 15.31 µm
50%: 36.04 µm
90%: 68.25 µm

Irregular,
non spherical

	Heat	Local weight gain	Global weight gain
0903-05	978±70 J/g	≈3.1 %	9.84 %
Big-size	113.5 J/g	0.75 %	2.21 %

© Fraunhofer ICT

COMPLETE OXIDATION AT DIFFERENT TEMPERATURES



<u>Oxidation experiments:</u>

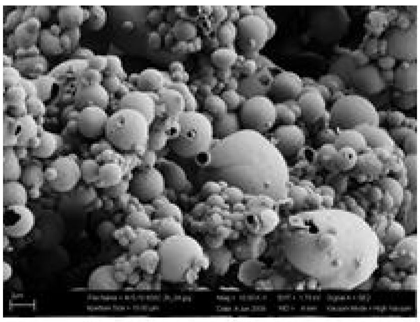
Exposure to temperature in air in a furnace
Powder: (0903-4) 31% 0-5µm 69% 5-10 µm
Temperatures:600°C, 650°C, 700°C, 800°C, 1000°C
Exposure times: 1 h, 2 h, 4 h, 60 h

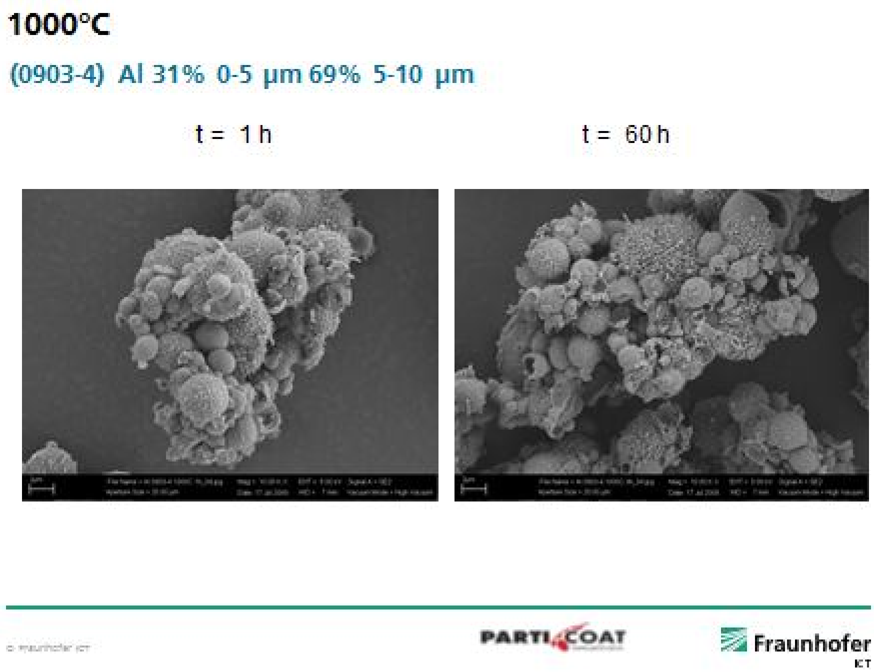
800°C

(0903-4) Al 31% 0-5 µm 69% 5-10 µm

t = 1 h

t = 2 h





Conclusions

- Below 800°C smooth gAl2O3 shells are achieved, however long oxidation times are needed
- Temperatures above 1100°C yield short oxidation times, whiskers structures on the surface
- Hollow alumina spheres are obtained, however sintered

➔ Alternative solutions were selected in WP8

Commercial alumina hollow spheres – alternative supplier

C.H. Erbslöh KG
Krefeld
Germany

1. SL 300 (d_{50}= 125 mm)
2. SL125 (d_{50}= 80 mm)
3. SL 75 (d_{50}=45 mm)

Al_2O_3 36-40%
Fe_2O_3 0.4-0.5 %
SiO_2 55-60%
TiO_2 1.4-1.6%

WP8 – Coating design and deposition on composites

Contribution to Coating design WP8

Objective:

Prepare different composite materials that are usually employed in construction for testing adherence with different binders.

Manufacturing of composites was done by vacuum infusion process, its low cost tooling and scalability to very large structures. It also minimizes the void contents inside the moulded composites, reduces VOC emissions, and results in less scrap than other moulding techniques.

ACCIONA has prepared:

- **Glass fibre composite with:**

1.- polyester resin
2.- fenolic resin
3.- Epoxy resin

- **Carbon fibre composite with**

1.- epoxi resin
2.- polyester resin
3.- fenolic resin

Best results were obtained with **epoxi resins, that also are the most commonly employed to fabricate materials with high structural requirements in flooring and walls**

Contribution to Coating design WP8

Objective:

To demonstrate the **importance of using hollow ceramic spheres** for the application of fire protection as a thermal barrier because of its **gas isolation effect**. Several powder to binder ratios were tested

Dechema e.V. has prepared two different kinds of powders to obtain the slurries based on Ceramabind 540 and **Hollow sphere shaped alumina-silica, and α-alumina flake** shaped powder

- Different binders have been tested. Finally, **binders based on inorganic materials** were selected. It would allow to avoid decomposition at temperatures above 400°C.

- **Low curing temperature binders** were selected, because at temperatures above 100°C the glass-fiber-epoxi laminates are damaged and their mechanical properties decrease

.

Table WP8.1: Summary of the most promising slurry compositions tested at Dechema e.V.

	reference	Ceramic powder (wt%)	Binder (wt%)
Stopping	IS001	40 Al_2O_3 flakes	60 ceramabind 540
	IS005	40 Al_2O_3-SiO_2 hollow spheres	60 ceramabind 540

Adherent and thick coatings were obtained after curing using both powders.

Contribution to Coating design WP8

- UC3M has investigated different ways of improving adhesion between the coating and the composite laminate through several atmospheric plasma treatments. The studies were carried out on two different surfaces epoxy resin and glass fiber reinforced polymer.

- It has been proved that this treatment reduces water contact of liquids increasing surface energy. This pre-treatment can promote the adherence of PARTICOAT slurries to composites.

- It has been demonstrated that the activation energy does not decrease after 1 month. Only in some cases, the polarity of the surface increases with time.

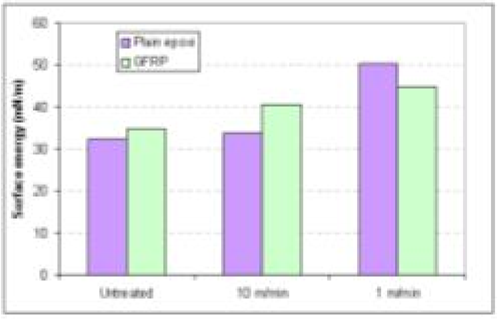


Fig. WP8.4: Surface energy. Two atmospheric plasma treatments. 10m/min and 1m/min.

Contribution to Coating design WP8

Fraunhofer has developed and tested different slurries.

- The selected binder was the commercially available PyroPaint 634 AS. This alumina-silica based advanced coating is rated for continuous service temperatures up to 1260ºC provides excellent adhesion to ceramic fiber blankets, modules and boards and resists wetting by nonferrous molten metals, increasing the durability and erosion resistance of the underlying material.

- An inorganic primer, based on Ethyl silicate, was applied between the composite and the alumina containing emulsion in order to Improve the adhesion between two phases.

Table WP8.2: Summary of the slurry compositions tested at Fraunhofer ICT

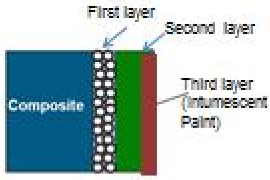
reference	Ceramic powder (wt%)	Binder (wt%)
IS006	15.22 (Al_2O_3 flakes)	Pyropaint 634AS
IS007	17.40 (Al_2O_3 flakes)	Pyropaint 634AS
IS008	44.13 (Al_2O_3 flakes)	Pyropaint 634AS

These fire protective coatings were deposited on composites at laboratory scale as described in the WP8 report.

Contribution to Deposition on Composites: WP8

Requirements Deposition Procedure

- Industrial applications at low cost.
- Large-scale production



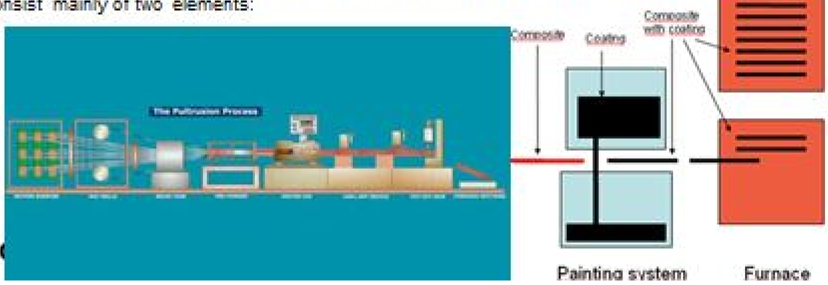
PARTICOAT Coatings drying requirements:

- Option 1: First layer: 2 hours at room temp. (preferred)
- Option 2: First layer: 2 hours at 100ºC.

- Second and third layer: Dry at room temperature (speed up the drying process using IR or microwave furnaces). Only few minutes.

PARTICOAT Solution:

The new coating deposition system will be directly coupled to the output of Pultrusion equipment and will consist mainly of two elements:



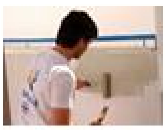
Contribution to Deposition on Composites: WP8

A number of furnaces in series avoid that this stage restricts the process.

Next layers will be directly applied in workshops where composite pieces are manufactured or also in situ, depending on the needs.

Some advantages of this two stage process:

- Well-finished composites pieces.
- Uniformity of the junctions of the different parts.



By hand: roller, brush….

Slow and inaccurate

By airless spray gun, realible and fast

Automatized robot systems

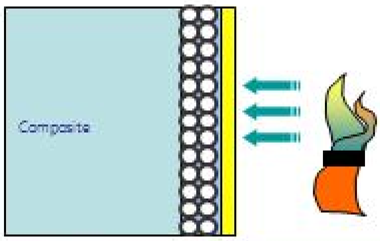
Summary

- Best results were obtained with epoxi based glass fibre reinforced composites.
- Improved adhesion, of coatings to composite substrates through several atmospheric plasma treatments.
- Final proposed systems: two and/or three layers design using hollow spheres and intumescent coatings.
- First aproach towards an industrial application system proposed. The prototype of a deposition procedure of a fire protective coating was thus delivered.

WP9 – Fire protection performance

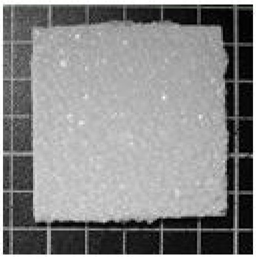
FINAL DESIGN

PMC 2 mm thick



- FRS + 10 % hollow spheres
- 1 mm thick

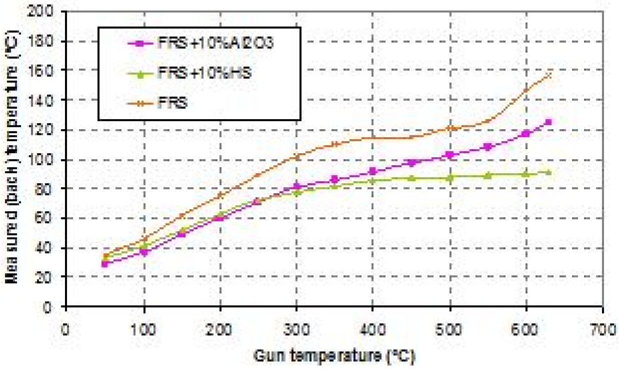
- Epoxy + Diammonium hydrogenphosphate (50/50)
- 2 mm thick



PARTICOAT

RESULTS PER ACTIVITY

- Low thermal conductivity
- Fire reaction
- Thermal barrier effect
- Mechanical resistance under loads

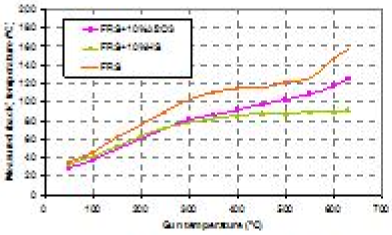


Increasing temperature tests up to 630°C

PARTICOAT

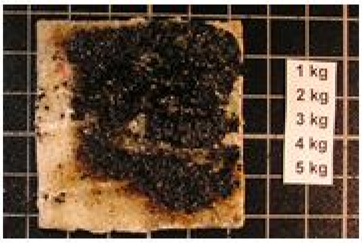
RESULTS PER ACTIVITY

- Low thermal conductivity
- Fire reaction
- Thermal barrier effect
- Mechanical resistance under loads



ASPECT

SCRATCH ADHESION TEST



PARTICOAT

RESULTS PER ACTIVITY

- Low thermal conductivity
- Fire reaction
- Thermal barrier effect
- Mechanical resistance under loads

PARTICOAT

RESULTS PER ACTIVITY

- Low thermal conductivity
- Fire reaction
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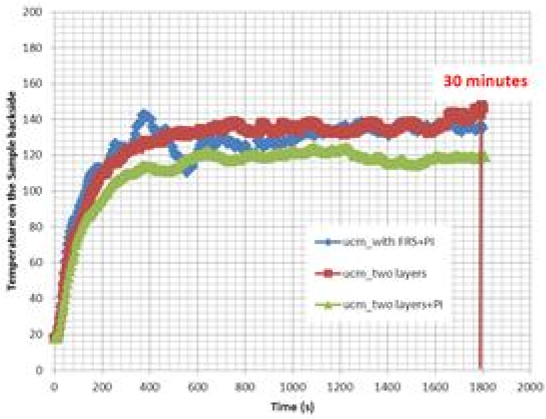
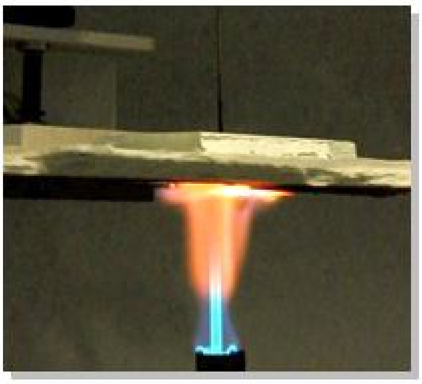


PARTICOAT

RESULTS PER ACTIVITY

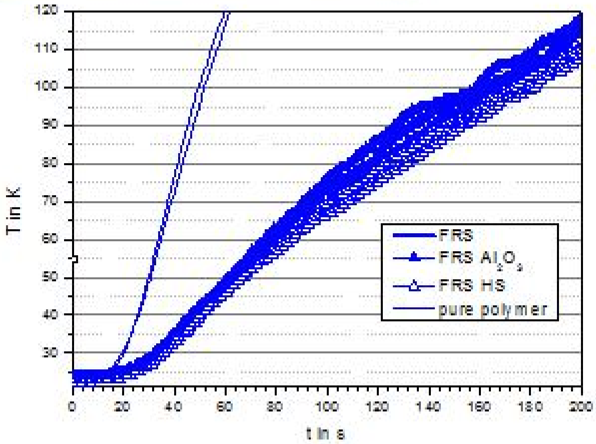
- Low thermal conductivity
- Fire reaction
- Thermal barrier effect
- Mechanical resistance under loads



PARTICOAT

RESULTS PER ACTIVITY

- Low thermal conductivity
- Fire reaction
- Thermal barrier effect
- Mechanical resistance under loads

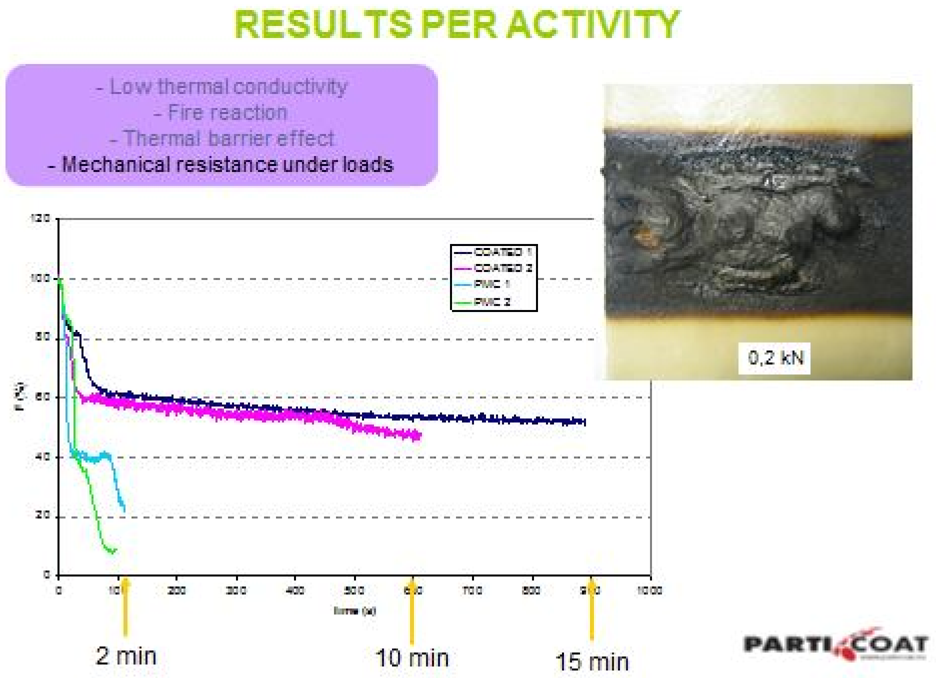


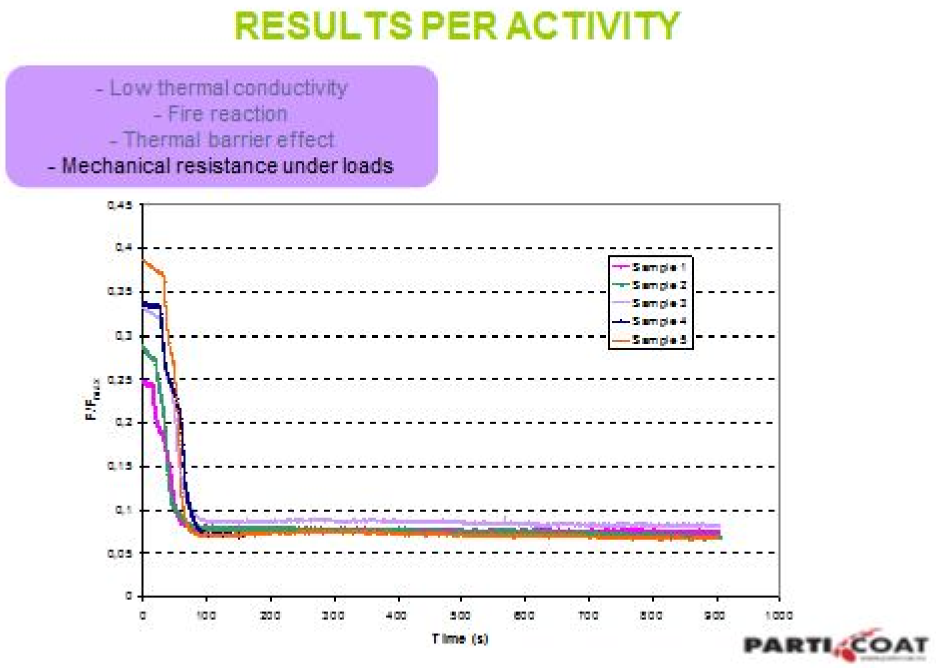
PARTICOAT

RESULTS PER ACTIVITY

- Low thermal conductivity
- Fire reaction
- Thermal barrier effect
- Mechanical resistance under loads

PARTICOAT





<u>Conclusions</u>

- Low thermal conductivity ⇒ Hollow spheres reduce it ⇒ good thermal isolation
- Fire reaction ⇒ Inflammable surface, inflammable drops (30 min) ⇒ excellent fire resistance
- Thermal barrier effect ⇒ Temperature decrease across the coating ⇒ good heat protection
- Mechanical resistance under loads ⇒ assured (40% of maximum load)

WP10 – Coating design and particle processing for electrical insulation

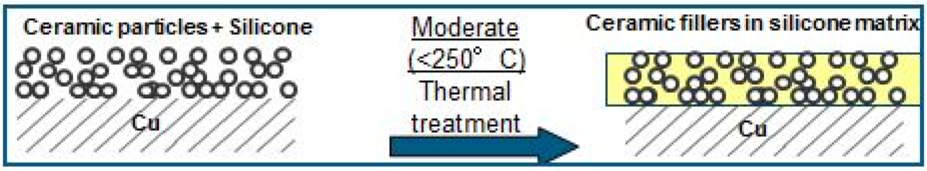
Introduction: Electrical Insulation of Copper Conductor

- Cylinder Water-cooled Tube
- Electrolytic pure Copper (99,95%)
- Operation Conditions:
  - Voltage 380 – 420 V
  - Current 6000 – 8000 A
- Environmental Conditions: Flames, dust, high temperature

Problem: Spark ignitions during the nickel production cause severe problems, leading to many stops

Aim: Provide a PARTICOAT based solution for electrical insulation and heat resistance of Copper in order to avoid spark ignitions

Coating design

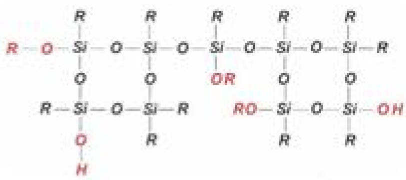


Insulating and high temperature behavior

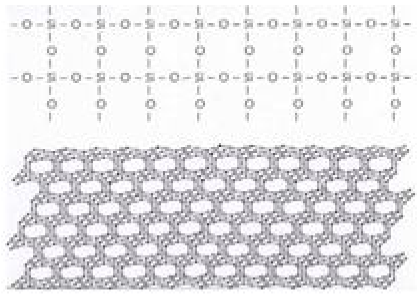
Different fillers and filling degrees of the silicone to be tested

Airbrush/Cu (sand blasted)/ZrO_2/Silicone/ 200° C/1h/Air/ ca. 200µm

Why Silicone?



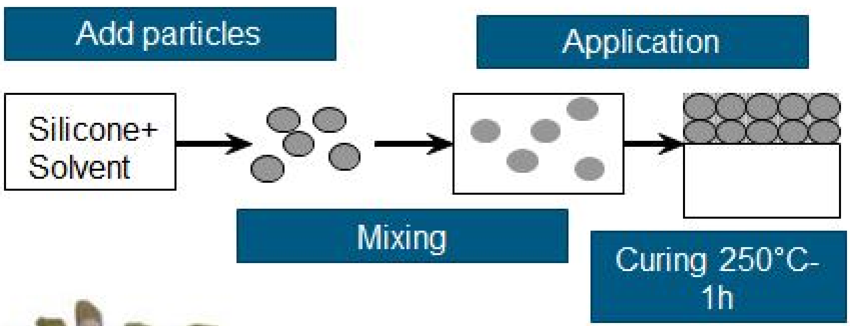
Low Temperature



Transformation at temperatures
> 500° C

Both are insulating

Manufacturing



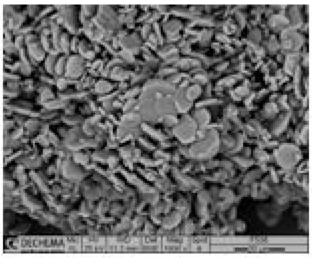
Viscosity is an issue!

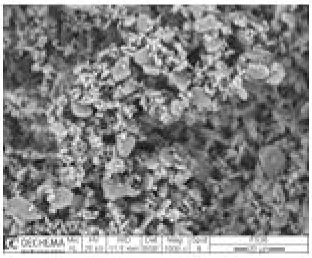
AirBrush does not work with
filler degrees considered necessary!

->Apply by painting!

1st Approach

Alumina



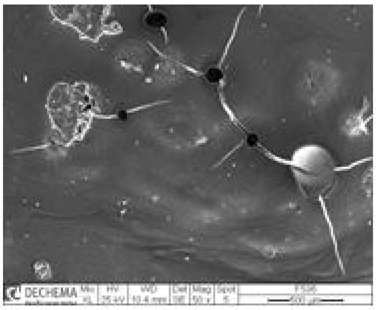


Different grain sizes/shapes

- Low shrinkage, high filling degree possible ~60 vol.% (in dry) and still paintable!

DECHEMA
Karl-Winnacker-Institut

Pure Alumina

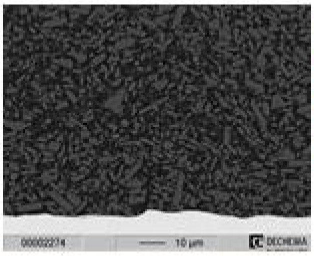


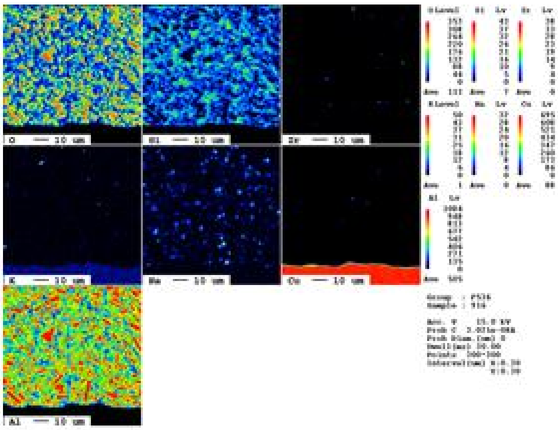
Different grain sizes -> finer particles less cracks after 250° C thermal treatment
- Need a very slow heating rate (or long drying at 90° C) not avoid air inclusions!
- Best particle size for the coating properties < 40 µm

DECHEMA
Karl-Winnacker-Institut

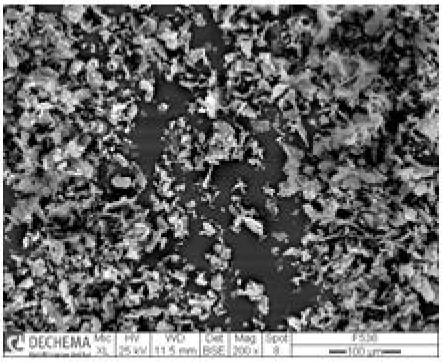
Alumina

300 ° C, 10 h





Mica – an extremly high electrical resistance

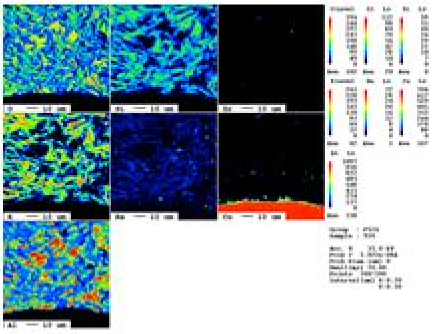


300° C , 10 h

50 vol.% filler: No bubbles, no cracks, high degree of filler possible!
Mica gives an extremly high electrical resistivity.

DECHEMA

Coating: Alumina particles + Mica

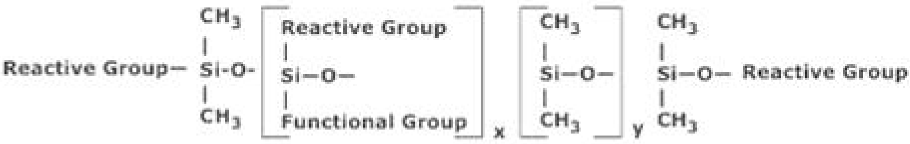



50 vol. % (1:1 Mica, Al2O3)
300° C, 10h
Extremely adherent (up to 300° C), high strength, no cracks
Shielding effect towards flames => Tested good as far as rheology, heat resistance, electric strength are concerned
BUT NEEDS HEAT TREATMENT!

DECHEMA

Roomtemperature crosslinking

Instead of crosslinking by temperature
-> add a chemical hardener



DECHEMA

Roomtemperatur-Hardening Materials

- Substitute the HT-hardened Silicon by RT Silicon + Hardener-system
- Increase the alumina content – lower the Mica

to and optimum 75:25 for higher abrasion behavior

Achieved crack free, stable coating, which can be applied by painting and a simple drying/hardening process.

WP11 – Deposition procedure for electric insulation

Methodology

In the framework of the PARTICOAT FP7 project, PyroGenesis had a critical role in developing an innovative electrical insulation coating, in collaboration with other project partners (Dechema, Fraunhofer ICT, Univ. Carlos III Madrid, Larco).
This new coating was developed to coat copper tubes conducting industrial electrical current of high voltage, in order to achieve electrical insulation and avoid spark ignitions.

The selection criteria, based on properties, as defined by Larco Metallurgical Company in Greece

1. Low to zero electrical conductivity (electrical resistance in the order of GΩ)
2. Fire resistance for 1-2 minutes
3. Good adhesion on the Cu substrate and structural integrity
4. Deposition procedure below 300°C
5. Resistance to particle erosion
6. Low cost raw materials and ease of preparation of the starting feedstock

Additional selection criteria

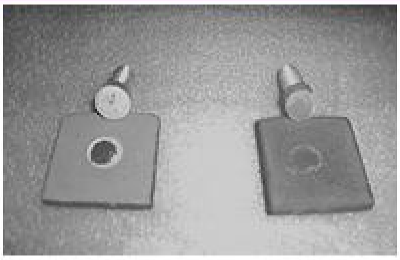
a. Ease of application (brushing or spraying)
b. No post - heat treatment if possible

Candidate materials

a. “Particoat” particles with Si-O semi-polymer as bonding material *(DECHEMA)*
b. Cu-Sn-A2O3 “Particoat” systems *(FRAUNHOFER ICT)*
c. Potassium Silicate emulsion with “Particoat” particles *(UCIIIM)*

PyroGenesis

Adhesion strength testing results: DECHEMA



D-AS: 29-34 MPa,
failure 80% adhesive and 20% cohesive

D-M: 18-23 Mpa,
failure 80% adhesive and 20% cohesive

<u>Erosion resistivity</u>

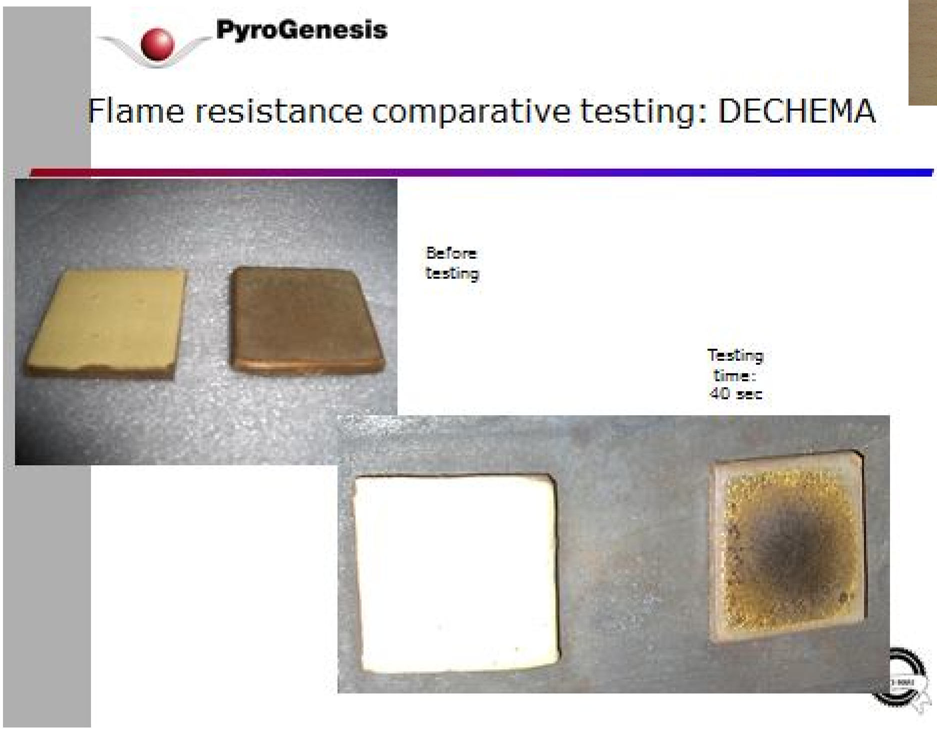
Adapted sand blasting system
Vertical flow of particles at the same point
Pressure: 3 bars
Testing time: 3-30 sec
Distance from coating's surface: 15 cm
Alumina particles, grit 18-24

PyroGenesis

Particle erosion comparative testing: DECHEMA

Flame resistance

Commercial flame generator system
Vertical flow of flame jet at the same point
Testing time: 40 sec
Distance from coating's surface: 10 cm
Flame jet diameter: 15 mm

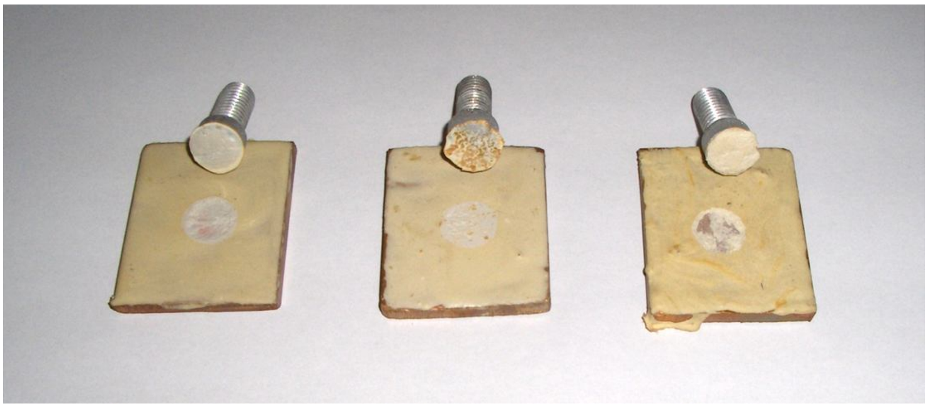


DECHEMA's approach (mainly coating based on alumina) is the most promising one for the final industrial application, since it responds very successfully to all property criteria
One major disadvantage:
Curing by heat treatment is needed. This can create serious technical difficulties in industrial scale application

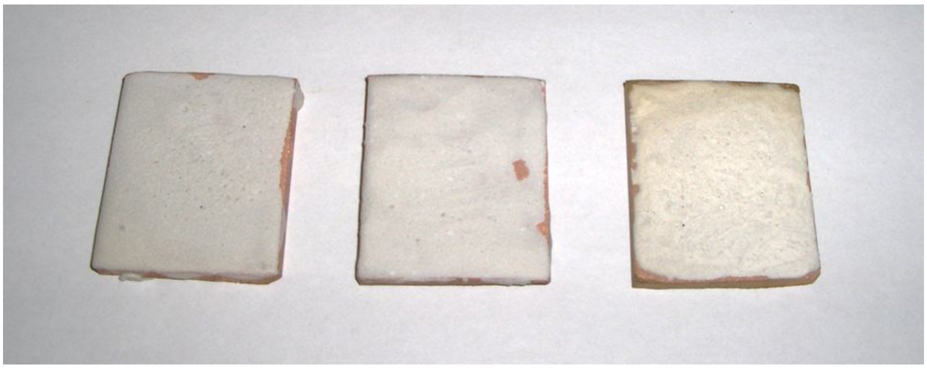
2^{nd} Approach

DECHEMA: 3 different new coatings 2 cured at room temperature, with *the same ceramic* and different hardener, and 1 heat treated

Adhesion strength:



Erosion resistance:



Flame resistance:

The finally selected coating, which was proposed and initially developed by partner **DECHEMA**, was a composite coating with silicone matrix and a mixture of ceramic particles.
NO NEED FOR HEAT TREATMENT

On site testing – 1st Test

- Standard D-formulation with hardener 1 was used
- High viscosity, very difficult application, need to add more liquids
- Brushing was practically impossible.
- Long time of application
- 3 meter Cu tube was coated and transferred by the furnace
- Feed back observation for 30 days

Conclusions from 1st test

The initially proposed coating's composition had to be modified in order to meet the industrial criteria:
Major criterion at the final application stage: time of preparation and time of application/curing
Problem: flow of material before curing.
Need for quick curing and for thin coatings
Old coating 100% removal (sand blasting) is a process demanding planning and time.

On site testing – 2nd Test

Application parameters to be tested:

a) Time and way of mixing
b) Time of achievement of min viscosity
c) Use of brushing necessary
d) Time of curing
e) Property criteria (3 tests in PYRO)

Conclusions from 2nd test

- Almost all coatings covered the property criteria
- **Major** criterion at industrial stage: **time of preparation and time of application/curing**
- Problem: flow of material before curing. Quick curing is necessary
- Old coating 100% removal (sand blasting) and surface preparation is a process demanding planning and time.
- **Hardener 2**, although less competitive in properties than hardener 1, gave shorter preparation and curing times
- The whole application plan must be well adapted to Industry's shut down plan. This means sudden stops and tight time frames

WP12 – Electrical insulation performance

Problem:

- Spark ignitions caused severe problems in the production of Nickel.
- In 2008, production of LARCO stopped 24 times due to spark ignitions.
- Stoppage times were about 8-36 hrs.
- The annual loss, caused these incidents, is around 5.000.000 $.
- In order to avoid spark ignitions a new innovative coating shall be applied in order to maintain the electrical insulation and heat resistant of copper conductor used for the power supply of EAF.

Situation:

- Cylinder Water-cool Tube (30 mm Internal Diameter – 50 mm External Diameter)
- Electrolytic pure Copper (99,95%) (commercial type Cu HCP)
- Operation Conditions: Voltage 380 – 420 V and Amperage 6000 – 8000 A
- Environmental Conditions: Flames – Dust – High Temperature.

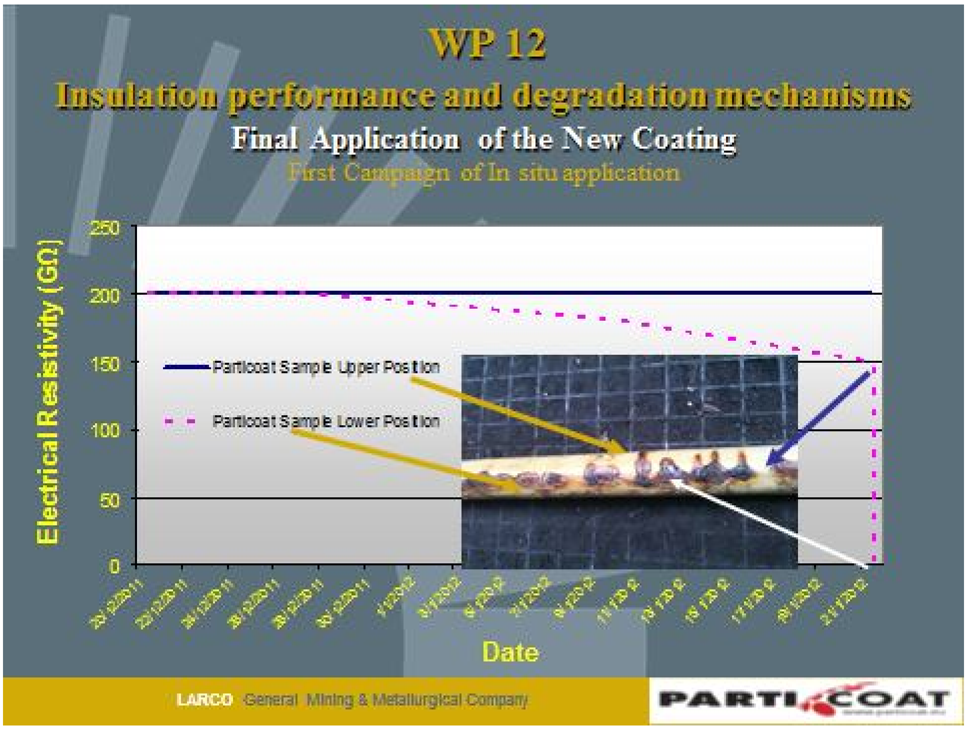
Copper tubes in the nickel metallurgy plant:

<u>Electrical insulation at high temperatures</u>

- Dechema samples presented excellent results according to all tests.
- The Dechema design coating prepared by the combination of Corundum and Mica was chosen for in situ application by brushing.
- Pyrogenesis prepared the best combination of DECHEMA coating for in-situ application.
- LARCO applied the final coating in field and monitoring the performance.

<u>In fiel testing – 1st test</u>

Duration 1 Month
Dechema Coating
Applied without water cooling
Applied without electrical current
Distance from the EAF roof was 80 cm

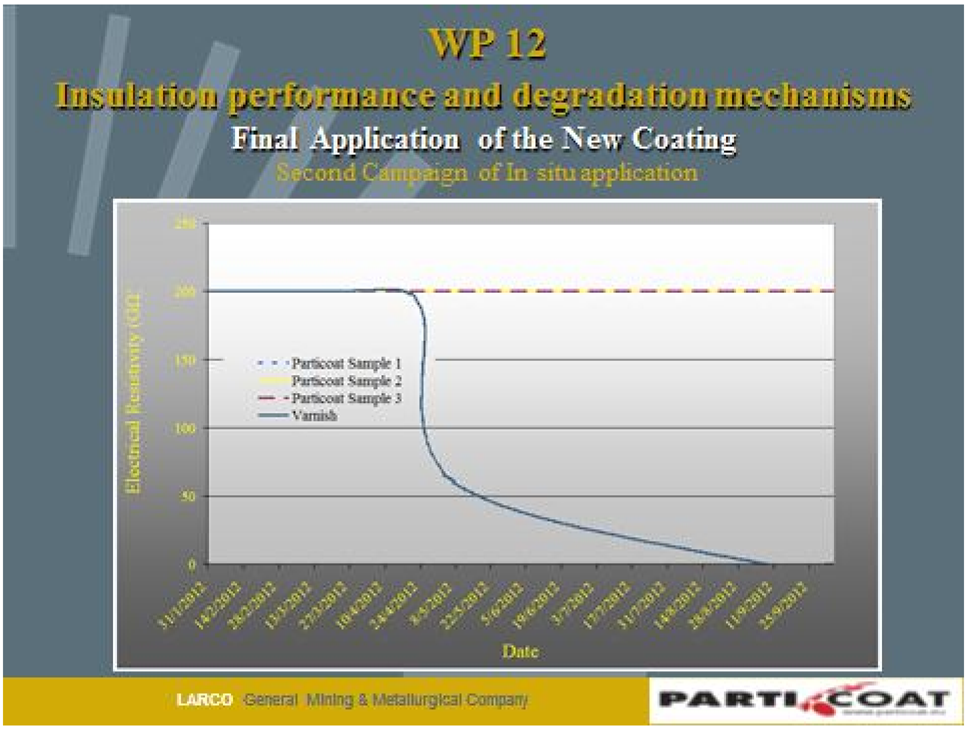


<u>Results</u>

Good Electrical Resistance.
The adhesion after one month was bad in some places due to the large thickness of the coating at these places.
The reason of adhesion failure was that during the brushing the coating slurry was not brushed equally on the pipe surface resulting in the formation of a coating with large thickness.

<u>In fiel testing – 2nd Test</u>

Start on February 2012 with Dechema coating
Applied on 6 Tubes with water cooling and electrical current
Distance from the EAF roof was 250 cm
Comparison with typical applied varnish
Total length 6 m



Results

- Good Electrical Resistance.
- The adhesion of particoat coating after 8 months in operation was good.
- After 3 months in operation, the adhesion of varnish coating gets weaker and in some places the electrical resistance starts to reduce. After 8 months the varnish coating doesn't present any electrical resistance.

Final in field tests

- Start on April 2012 with modified by Pyrogenesis Dechema coating
- Applied on 12 Tubes with water cooling and electrical current
- Distance from the EAF roof was 300 cm
- Total length 30 m

Results

- The adhesion of particoat coating after 5 months in operation was excellent.
- The electrical resistance after 5 months in operation was excellent, too.

Conclusions

1. The final coating present very good performance in terms of Electrical resistance and adhesion.
2. In comparison with the varnish applied up to now the performance of new coating is much better.
3. The production of the coating slurry must be very careful in order to achieve a successful application.

WP13 – Achievements and advance evaluation

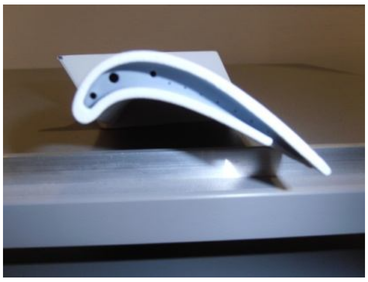
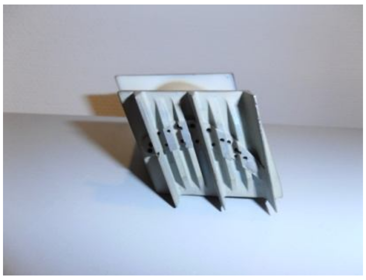
Siemens:

Particoat results which can be applied in turbines

- New aluminization process (no hazardous binder)
- Formation of a TBC system based on small Aluminide particles
- Formation of stable anorthide phases based on chemical reactions between Aluminide particles and CMAS against CMAS attack
- First results on SPPS TBC systems
- New bondcoat approach based on milled MCrAlY powders

New aluminization process (no hazardous binder)

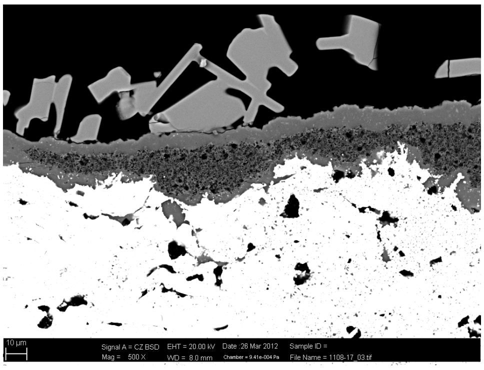
- Application possible on different turbine components
  Tip bottom aluminization
  Outer shroud aluminization
  Rotor aluminization


More basic investigation necessary (new development project)

Protection agains CMAS

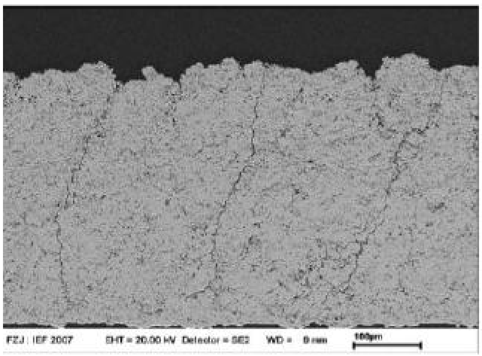
Formation of stable anorthide phases based on chemical reactions between Aluminide particles and CMAS against CMAS attack
Protective anorthide formation on top of PSZ TBC (CMAS protection)



Internal Siemens project available; Partner: Fraunhofer Institute, FZ-Jülich
Implementation after final R5 Review; Time schedule: ~ 4-5 years

SPPS TBC systems

- First results show that the application is possible
- Life time must be expanded



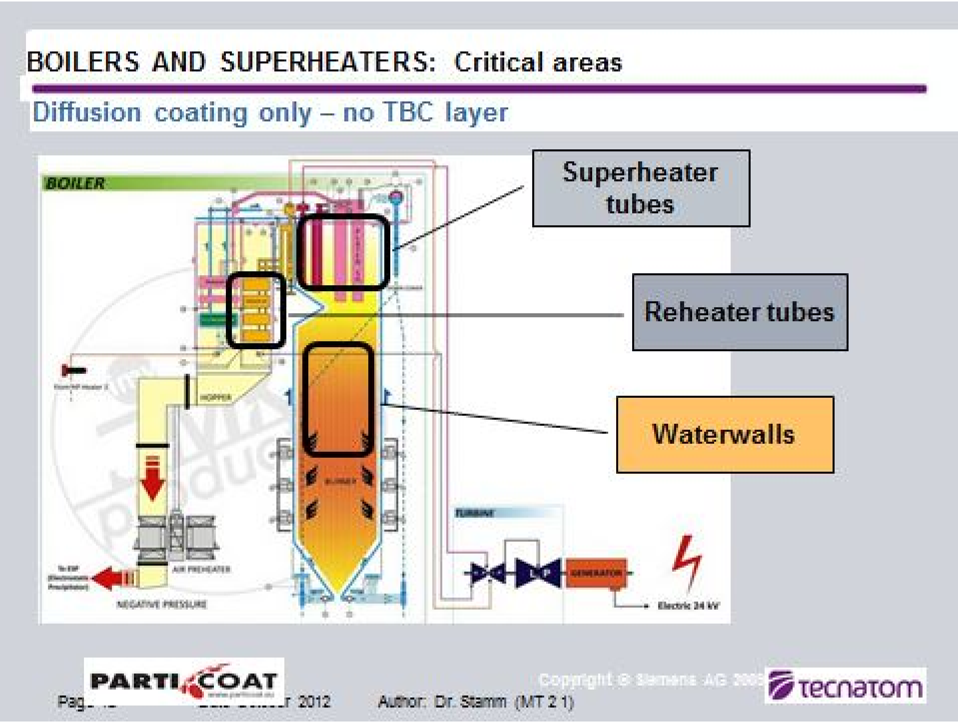
Internal Siemens project available; Partner: Fraunhofer Institute, FZ-Jülich
Preparation of a visibility study; Possible test run in about 5 years

New bondcoat approach based on milled MCrAlY powders

- HVOF sprayed milled powder shows good results

No actual Siemens project available; Will be included in the materials road map for future projects; Implementation depends on Review results

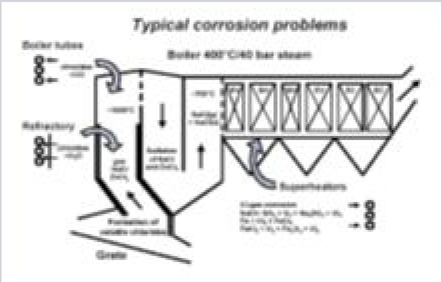
<u>TECNATOM</u>:



WATERWALLS

Corrosion (especially on the fire side) due to:
- Deposits of fly ash
- Accumulation of alkali and sulfur species

Thermal fatigue due to:
- Multiple cyclic strains that exceed the fracture strain of the fire-side oxide.



PARTICOAT

Experiments developed within the project, including different types of coatings, substrates and deposition procedures

APPLICATION	PARTNERS	SUBSTRATE	COATING	PROCEDURE
High Temperature Protection Fire Protection Electrical Insulation	Fraunhofer ICT Dechema SVUM UC3M ULR Acciona Turbocoating Larco Pyrogenesis	Iron based Alloys - AISI 304 - AISI 321 - AISI 347/347H - AISI 446 - P91 - 16 Mo Ni based Alloys - Pure Ni - Ni20Cr - IN738LC - PWA1483 - CM247 - René N5 Composite Material - GFREP Copper - HCP Cu	Multisize µm-Al particles Al-Si slurries Al + B additions Alumina hollow spheres Potassium Silicate + Particoat particles Cu-Sn-Al2O3 Particoat systems Particoat particles + Si-O polimer Corumdum + Mica	Rolling dipping Spraying Brushing Sol-gel

MAIN BENEFITS:

- Use of common coating deposition procedures (which reduces the manufacturing cost) such as:
  - Spraying
  - Brushing

    - Rolling dipping
    - Sol-gel
- Non special requirements regarding equipment to be used.
- Improvement of the properties:
    - Extension of the overhaul interval
    - Development of suitable coatings that would allow the use of low cost steels.