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

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Name of the scientific representative of the project's co-ordinator¹, Title and Organisation:
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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

PARTICOAT concept

Production of source metal particles by PMT and FCC
Spherical metal particles with defined size

Deposition by brushing, spraying, sintering, anig-gel

Heat treatment by pre-treatment oxidation sintering diffusion

Coating with gap-free top coat and diffusion layer

Development of suspensions for the PARTICOAT slurry:

“GREEN” COATING: Suspension

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>Plasticizer</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly ethylene glycol (PEG)</td>
<td>Methyl cellulose (MC)</td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycol (PEG)</td>
<td>Poly vinyl alcohol (PVA)</td>
<td></td>
</tr>
<tr>
<td>Glycerol (G)</td>
<td>PVA (OH)</td>
<td></td>
</tr>
<tr>
<td>NH-4A</td>
<td>Poly acrylic acid (PAA)</td>
<td></td>
</tr>
<tr>
<td>Primal 1500</td>
<td>Ammonium polyacrylate (NH-4A)</td>
<td></td>
</tr>
<tr>
<td>Dispers A-40(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Evaporation T decreases
- Dextranilamine
- Alkali metal silicate

Source particles
- Potential isoelectric point

Mixing
- Strength
- Density
- Viscosity
- Strength
- Gel limitation

Drying
- Pseudo-plastic
- Rheology study
- Viscosity
- Shear rate

Development of suspensions for the PARTICOAT slurry:

© macrofotograf
**Thermal treatment**

![Diagram showing thermal treatment process]

**Work flow chart for the PARTICOAT design**

![Diagram showing work flow chart for PARTICOAT design]

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**“GREEN” COATING**

Base powder: Al 3-5 μm, 10-25 μm, 30-60 μm

**CHARACTERIZATION**

Thermal stability
Diffusion
100, 300, 1000 h
metallography
HTXRD

---

**THERMAL TREATMENT 1**

400-500 °C
1, 2, 4 h
XRD, TGA, metallography

**THERMAL TREATMENT 2**

600, 700, 800, 900, 1000 °C
5 h
TGA, metallography

**THERMAL TREATMENT 3**

---

Binder: PEO, PVA, Pahl
Al/Bi ratio = 1:1.5
Dispersant, Z potential
Rheology: Viscosimeter
*Designs for special applications – graded structures and surface sealing*

**Gas turbine**
- TBC sacrificial coating from μm/nano-Al₂O₃

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

---

![Image](image-url)
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

Method – electrical explosion of wires (EEW)

<table>
<thead>
<tr>
<th>Characteristics of EEW machine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Explosion chamber</td>
</tr>
<tr>
<td>2. Powder filter</td>
</tr>
<tr>
<td>3. Powder collector</td>
</tr>
<tr>
<td>4. High-voltage circuit</td>
</tr>
</tbody>
</table>

\[ C - \text{capacitor} \]
\[ L - \text{inductance} \]
\[ R - \text{resistor} \]
\[ S - \text{switch} \]
\[ EW - \text{exploding wire} \]

The effectiveness of electrical energy transformation is more than 0.85

AI nanopowder, produced with EEW technology
The scheme of plasma-spray equipment for synthesis of nano-powders:

1 – diers; 3 – reactor; 5 – plasma generator; 4 – high-frequency generator; 6 – filter; 7 – condenser; 8 – scrubber; 9 – 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.

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

**SIEVE SIZE: 0903-4**

- $D_{10} = 0.82 \mu m$
- $D_{50} = 2.14 \mu m$
- $D_{90} = 4.01 \mu m$

Specific 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

DoW for WP 4:
Coating manufacturing procedure

VISCOSITY- CONE-PLATE VISCOSIMETER

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

Investigated particles and experiments

High temperature X-ray diffraction

Heating in air

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Material</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 31% &lt;5 μm 51% 5-19 μm</td>
<td>powder on Pt-holder (0003-4)</td>
<td>RT – 1000°C, ΔT=25°C</td>
</tr>
<tr>
<td>Al 31% &lt;5 μm 51% 5-19 μm + PEG on Aluchrom Y Hf (0503-4)</td>
<td>400°C – 1200°C, ΔT=25°C</td>
<td></td>
</tr>
<tr>
<td>Al 0.3 – 0.7 μm + PEG on Aluchrom Y Hf</td>
<td>RT – 1100°C, ΔT=25°C</td>
<td></td>
</tr>
<tr>
<td>Al 2 – 5 μm + PEG on Aluchrom Y Hf (0211-19)</td>
<td>400°C – 1200°C, ΔT=25°C</td>
<td></td>
</tr>
<tr>
<td>Al 30 – 50 μm + PEG on Aluchrom Y Hf</td>
<td>RT – 1350°C, ΔT=50°C</td>
<td></td>
</tr>
</tbody>
</table>

Isothermal in air

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Material</th>
<th>Temperature and Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 31% &lt;5 μm 51% 5-19 μm + PEG on Aluchrom Y Hf (0003-4)</td>
<td>3 h at 650°C, 650°C, 1000°C</td>
<td></td>
</tr>
<tr>
<td>Al 31% &lt;5 μm 51% 5-19 μm + PEG on Aluchrom Y Hf (0903-4)</td>
<td>24 h 800°C</td>
<td></td>
</tr>
</tbody>
</table>
(0603-4) 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

Fraunhofer ICT

(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

Fraunhofer ICT
Oxidation mechanism of nano- and μ-Al particles

Transformation: γ-Al₂O₃ → α-Al₂O₃ above 850°C

High disorder structure, cubic-fcc

Ordered structure, hexagonal close packed oxygen lattice

Higher atomic density

Volume shrinking about 11.8%

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

Tailoring the heat treatment

Example: slurry made of H₂O + 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)
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, AISI 347, 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
**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 topcoat
- Ductility of the diffusion layers

Multiple size 1-20 µm Al + 20% B

⇒ Similar results

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**DEHEMA**

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

Increasing time allows to obtain the oxidised hollow spheres top coat + Fe-rich aluminides (less brittle)
**Main methodology of investigation:**

- **Materials:** Pure Ni, Ni20Cr, IN-738LC, PWA-1483, CM-247, Ni5 (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

---

**Pure nickel as model substrate**

**Aluminization onto pure Ni:** influence of the temperature

OP-5 polishing (0.1 μm) metal finish

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Duration</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>650°C</td>
<td>2h</td>
<td></td>
</tr>
<tr>
<td>700°C</td>
<td>2h</td>
<td></td>
</tr>
<tr>
<td>700°C</td>
<td>2h + 1100°C</td>
<td>2h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>From 3 μm to 6μm on average</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Columnar grains after full TT</td>
</tr>
</tbody>
</table>
**Need of tailoring in superalloys: thermodynamics**

- **Modeling**
  - β-NiAl
  - Precipitates (Cr, W, Mo, Re)

**Superalloys and 6 μm Al particles**

- 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

T°C

Sputtering
Slurry spray
Sintering + diffusion
Binder evaporation
Top coat oxidation + bond coat microstructure

Pt RE (Y, Zr, Hf)

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 $800^\circ$C in air (I)

- AISI 446 (ferritic)/Al/1050h
- AISI 446 (ferritic)/Al-Si/300h

- Diffusion zone of mainly FeAl(Cr)
- DL cracks through grain boundaries
- Thick inter-diffusion layer (Al diffusion)
- SiO$_2$/Al$_2$O$_3$ based top coat
- Diffusion zone of FeAl-Si (3% At.)
- Cr$_3$Si precipitates continuous layer
- Thin inter-diffusion layer

Characterization after exposure at $800^\circ$C in air (II)

- AISI 446/Al/1050h
- AISI 446/Al-Si/300h

- Al inter-diffusion strongly related to Cr$_3$Si presence
Characterization after exposure at 800°C in air (III)

- Similar top coat thickness and composition as observed for ferritic substrates.
- TGO of Al₂O₃ 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.)
- Cr₂Si does not form a continuous layer

Characterization after 600°C

- No chlorine species are detected in the diffusion zone.
- Phases present in the 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**

- 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**

- Diffusion layer is thicker for Al based coatings
- Chlorine species detected in diffusion zone
- Weight gain increased due to re-healing of cracks by Al₂O₃
- 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$_3$Si between the diffusion and inter-diffusion layer
  • Si addition increases inter-diffusion for austenitic substrates due to the stabilization effect of ferritic phase.

SVUM

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$_2$O
• Al particles 3 – 5 µm
• Deposition: deep coating 200 – 300 µm thick layer
• annealing: 800 ºC/8 h, air

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

![Coating manufacture: Coatings for corrosion tests](image-url)
Laboratory tests – atmosphere: results

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

Laboratory tests – deposit: results

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

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 (crosssection measurements)

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
WP5.1.2 Oxidation of Ni-based alloys

Isothermal oxidation

**Isothermal oxidation of superalloys: single Al**

Isothermal at 1100°C for: René N5 (red) and PWA-1483 (blue)

- Top coat adherent in all substrates except when extensive TiO₂ segregation at TGO. No rumpling compared to Sneca-type coatings
- Degradation occurs by βNi₃Al → γ′Ni₃Al transformation
- Last 5R2 than in conventional Sneca-type coatings (greater mechanical stability)

**CM-247 (groen)**

- 300°C/100h
- 1000°C/500h
- 1100°C/100h

**Isothermal oxidation of superalloys:**

Single Al + water vapour

- No influence of water vapour on the oxidation resistance
- Particoat should be resistant to exhaust combustion gases & condensation effects

**René N5 at 1100°C**
Graded structures

Isothermal oxidation of superalloys:
with interlayer in air

- Interlayer limits however segregation of detrimental elements to the TGO
- No secondary reaction zone (SRZ) either. However, much greater oxidation kinetics.

Isothermal oxidation of superalloys:
with multi-size Al

- Greater adherence of the top coat than with multi-size Al
Isothermal oxidation of superalloys:
Exposure at 1000°C in air and SO₂-containing synth. air

- Pack aluminization shows lowest weight gain
- Al-Si coatings lower weight gain than Al coatings
- Coatings without top coat lower weight gain (top coat oxidation)
- Exposure in SO₂ increases weight gain
- Coatings without top coat lower weight gain
- Al coatings lower weight gain than Al-Si coatings (after 800 hours)

Isothermal oxidation of superalloys:
Characterization after exposure in SO₂ at 1000°C

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

- Top coat adherent even under high pressure
- Local attack in Al-based slurries but no attack of the substrate
- Particulates should resist in hot corrosive environments too
Cyclic oxidation

Cyclic oxidation of superalloys: single Al

René N5 at 1100°C

PWA-1483 at 1100°C

PWA-1483 at 1000°C

- Cyclic oxidation resistance depends on coating composition. If too much TiO₂ (PWA-1483 great spallation), otherwise Partcoat behaves similarly to pack cemented coatings.
- Adapt coating/substrate to operating temperatures.

Cyclic oxidation of superalloys: with multisize Al

IN-738 + 1080°C/air (23 h cycle)

- Multisize Al does not impede TiO₂ segregation that brings about partial detachment of the top coat.
Fraunhofer ICT: Cyclic oxidation of superalloys with special design coatings

<table>
<thead>
<tr>
<th>Test program</th>
<th>Substrate</th>
<th>Bond coat</th>
<th>1. layer</th>
<th>2. layer</th>
<th>Lifetime (cycles x 23h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference sample (Siemens)</td>
<td>IN738LC</td>
<td>SC2464</td>
<td>YSZ</td>
<td>—</td>
<td>41.5 cycles</td>
</tr>
<tr>
<td>1</td>
<td>IN738LC</td>
<td>SC2464</td>
<td>3YSZ [90-110 µm]</td>
<td>YPSZ [500 µm]</td>
<td>67 cycles</td>
</tr>
<tr>
<td>2</td>
<td>IN738LC</td>
<td>SC2464</td>
<td>3YSZ [560-660 µm]</td>
<td>—</td>
<td>56 cycles</td>
</tr>
<tr>
<td>4</td>
<td>IN738LC</td>
<td>SC2464</td>
<td>Al2O3/14ZrO2 [460-550 µm]</td>
<td>—</td>
<td>19 cycles</td>
</tr>
<tr>
<td>5</td>
<td>IN738LC</td>
<td>SC2464</td>
<td>YPSZ [530-550 µm]</td>
<td>—</td>
<td>80 cycles</td>
</tr>
</tbody>
</table>
Degradation mechanisms

Image analysis: method 1/3 – define window of analysis

Follow-up of:
- Phase transformations $\beta$-NiAl $\rightarrow$ $\gamma'$-Ni$_3$Al
- Thickness of the coating sub-layers
- Extension of the SRZ
- Fraction of precipitates

Analysis window 130 $\times$ 250 $\mu$m

Image analysis: method 2/3 – differentiation

$\beta$ NiAl areas

Phase transformation fraction assessment

$\gamma'$-Ni$_3$Al “pockets”

Evolution of precipitates amount (TCP) / strengthening elements

SRZ formation / extension

Mechanical stability
Coating / substrate
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 SO₂).
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 SO₂ containing atmosphere:
   • Al-Si produced coating have shown excellent protection in SO₂ 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.
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% Na₂SO₄ - 60% V₂O₅

Conditions
- Atmosphere: Air
- Heating rate: 10°C/min
- From RT to 675°C (temperature thermocouple)

Interaction of the PARTICOAT coating with molten deposits

40% Na₂SO₄ and 60% V₂O₅ 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
PARTICOAT reacts with V and prevents its penetration to the metal surface.
Lotus effect not observed, molten deposit infiltrates the topcoat.
Introduction

Concept and design

*New multipurpose coating system based on novel particle technology for extreme environments at high temperatures*

*Innovative idea of a combined diffusion bond coat and thermal barrier top coat in a single step coating process*

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

Top coat producing aluminium particles
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
Conclusions

- 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:

**Thermal barrier effect: Epiradiator**

Experimental set-up for measuring the thermal barrier effect

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 $\gamma$- and $\theta$-Al$_2$O$_3$ 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.
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 % H₂O)

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

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

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)

Lanzarote 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

800 °C, aluminium bath

16Mo3/1 min

16Mo3/10 min

347H/1 min

347H/10 min
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

<table>
<thead>
<tr>
<th>Composition of fly ash (wt. %)</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.80</td>
<td>1.60</td>
<td>1.65</td>
<td>1.28</td>
<td>3.00</td>
<td>0.26</td>
<td>7.00</td>
<td>0.24</td>
<td>0.01</td>
<td>1.20</td>
<td>0.57</td>
</tr>
</tbody>
</table>
**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/SO₂ 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
- Testvolume: 1m³

SAMPLES LOCATION

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

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

**THICKNESS MEASUREMENT**

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

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>THICKNESS B (µm)</th>
<th>THICKNESS E (µm)</th>
<th>THICKNESS B (µm)</th>
<th>THICKNESS E (µm)</th>
<th>SEM Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>B321 (W2C)</td>
<td>168</td>
<td>138</td>
<td>142</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>IN309 (W2C)</td>
<td>102</td>
<td>100</td>
<td>101</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>PH4-L (W2C)</td>
<td>214,4</td>
<td>218</td>
<td>218,5</td>
<td>218,5</td>
<td></td>
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<tr>
<td>AISI4732 (W2C)</td>
<td>157,2</td>
<td>157,2</td>
<td>157,2</td>
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<tr>
<td>AISI4733 (W2C)</td>
<td>171,3</td>
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<td>AISI4743 (W2C)</td>
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<tr>
<td>4058A-480 (W1C)</td>
<td>50</td>
<td>50</td>
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<tr>
<td>4022B0 (W2C)</td>
<td>84</td>
<td>84</td>
<td>84</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

**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

![Diagram of APS-TBC Life Time Prediction](image)

APS-TBC: Life Time Prediction

Finite Element Methods (FEM) allow simulating stress states and deformation inside the individual layers.

Incubation phase

- The crack length is assumed to grow linearly with TGO until TGO thickness of 1% TGO thickness at the end of the incubation phase equals 1% of wavelength of the roughness profile of the bondcoat.

- Energy release R have two major sources:
  - G1: Impact of thermal mismatch (elastic behavior) - Delamination
  - G2: TGO: Reflects the contribution by lateral growth of TGO

Calculation of crack length

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.

- The stress reaches approx. 1/4 of the averaged peak-to-peak roughness of the bondcoat Rz.

Approach for life prediction
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

- 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 cm², 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.

Case study: Life Cycle Inventory Analysis

Option A: Chemical Vapor Deposition
Option B: Pack Aluminizing
Option C: Atmospheric Plasma Spraying (APS)
Option D: PARTICOAT Process: Dechema, La Rochelle, Fraunhofer

Chemical Vapor Disposition

- Use of coating
- Characterization of coating
- End of Life
- Coating
- Feedstock Material
- Feedstock Material
- Neutralization
- Chemical Vapor Deposition
- Surface Preparation
- Degreasing
- Grit Blasting
- Cooling water
- Electricity
- Pumping
- Solid waste
- Air Emission
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


Considered Factors

- Climate Change: Use of Electricity
- Human Toxicity: Use of alumina powder in sandblasting / 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)
Conclusions

- Heat treatment is the most relevant process in the coating technologies analyzed due to the high energy requirement.
- Quantities of raw materials are small compared 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 the 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

TG/DTA Study of the oxidation of µm-Al particles

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 - 950°C ; 1-10-24 h
Temperature / time: 1050°C – 1150°C - 1250°C ; 10 h
0903-05, 09030-4, commercial atomized powders
Temperature / time: 750 ºC ; 1 h

Reproducibility:

HEATING PEAKS’ ANALYSIS: COMPARISON WITH BIG-SIZE POWDERS

Big-Size Powder
10%: 15.31 µm
50%: 36.04 µm
90%: 68.25 µm
Irregular, nonspherical

<table>
<thead>
<tr>
<th></th>
<th>Heat</th>
<th>Local weight gain</th>
<th>Global weight gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0903-05</td>
<td>978±20 µg</td>
<td>≈3.1 %</td>
<td>9.84 %</td>
</tr>
<tr>
<td>Big-size</td>
<td>113.5 µg</td>
<td>0.75 %</td>
<td>2.21 %</td>
</tr>
</tbody>
</table>

© maurocheri
Oxidation experiments:

Exposure to temperature in air in a furnace

Powder: \((0903-4)\) 31% 0-5 µm 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 \hspace{1cm} 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. Erbslöhn KG
Krefeld
Germany

1. SL 300 (d50= 125 mm)
2. SL125 (d50= 80 mm)
3. SL 75 (d50=45 mm)

Al2O3 36-40%
Fe2O3 0.4-0.5 %
SiO2  55-60%
TiO2  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. epoxy resin
  2. polyester resin
  3. fenolic resin

Best results were obtained with epoxy 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 Caramind 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-epoxy laminates are damaged and their mechanical properties decrease.

<table>
<thead>
<tr>
<th>Table WP8: Summary of the most promising composition tests at Dechema e.V.</th>
</tr>
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<tbody>
<tr>
<td>Reference</td>
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<tr>
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<td>Stoping</td>
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</table>

Adherent and thick coatings were obtained after curing using both powders.
Contribution to Coating design WP8

IC3M 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.

![Graph showing surface energy] (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 1260°C 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 |
|---------------------------------|-----------------|-----------------|
|                                 | Ceramic powder  | Binder (wt%)    |
| **IS006**                      | 15.20 (Al₂O₃, flakes) | Pyropaint 634 AS |
| **IS007**                      | 17.40 (Al₂O₃, flakes) | Pyropaint 634 AS |
| **IS008**                      | 44.13 (Al₂O₃, flakes) | Pyropaint 634 AS |

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

**PARTICOAT Solution:**

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

**RESULTS PER ACTIVITY**

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

Graph showing increasing temperature tests up to 630°C.
RESULTS PER ACTIVITY

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

ASPECT

SCRATCH ADHESION TEST

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
RESULTS PER ACTIVITY

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

- Low thermal conductivity $\Rightarrow$ Hollow spheres reduce it $\Rightarrow$ good thermal isolation
- Fire reaction $\Rightarrow$ Inflammable surface, inflammable drops (30 min) $\Rightarrow$ excellent fire resistance
- Thermal barrier effect $\Rightarrow$ Temperature decrease across the coating $\Rightarrow$ good heat protection
- Mechanical resistance under loads $\Rightarrow$ 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: 0000 – 0000 A
- Environmental Conditions: Flames, dust, high temperature

**Problem:** Spark ignitions during 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**

<table>
<thead>
<tr>
<th>Ceramic particles + Silicone</th>
<th>Moderate (&lt;250°C) Thermal treatment</th>
<th>Ceramic fillers in silicone matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td></td>
<td>Cu</td>
</tr>
</tbody>
</table>

**Insulating and high temperature behavior**

Different fillers and filling degrees of the silicone to be tested

Airbrush/Cu (sand blasted)/ZrCu/Silicone/200°C for 1h/Atm/pe 200μm
Why Silicone?

Low Temperature

Both are insulating

Transformation at temperatures > 500°C

Manufacturing

Add particles

Silicone + Solvent

Application

Mixing

Curing 250°C - 1h

Viscosity is an issue!

AirBrush does not work with filler degrees considered necessary!

-> Apply by painting!
1\textsuperscript{st} Approach

**Alumina**

Different grain sizes/shapes

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

---

**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 \( \mu \text{m} \)
Alumina

300° C, 10 h

Mica – an extremely high electrical resistance

300° C, 10 h

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

Roomtemperature crosslinking

Instead of crosslinking by temperature
-> add a chemical hardener

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)

Adhesion strength testing
Adhesion strength testing results: DEHEMA

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

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

Erosion resistivity
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

Particle erosion comparative testing: DEHEMA
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
2nd 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

Copper tubes in the nickel metallurgy plant:

Electrical insulation at high temperatures

- 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.

In field testing – 1st test

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

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.
In field testing – 2nd Test

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 againsts 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

TECNATOM:
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.

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

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

<table>
<thead>
<tr>
<th>APPLICATION</th>
<th>PARTNERS</th>
<th>SUBSTRATE</th>
<th>COATING</th>
<th>PROCEDURE</th>
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</thead>
<tbody>
<tr>
<td>High Temperature</td>
<td>Fraunhofer ICT</td>
<td>Iron based alloys</td>
<td>Multialkyl-A particles</td>
<td>Rolling cladding</td>
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<td>Protection</td>
<td>Doehmns</td>
<td>AISI 304, AISI 1018, AISI 347, AISI 440, 18 Ni</td>
<td>Al-Bilayers</td>
<td>Spraying</td>
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<td>SVUM</td>
<td>18 Ni</td>
<td>18 Ni</td>
<td>Brushing</td>
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<td></td>
<td>UC3M</td>
<td>Ni based Alloys</td>
<td>Al + B additions</td>
<td>Spi-gel</td>
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<td>UUR</td>
<td>Pure Ni</td>
<td>Alumina hollow spheres</td>
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<td>Actonla</td>
<td>NiCoCr, NiCrAl</td>
<td>Potassium Silicate +</td>
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<td></td>
<td>Turbocoating</td>
<td>CrAlY</td>
<td>Partcoat particles</td>
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<td>Lanco</td>
<td>CrAlY</td>
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<td>Partcoat particles + SiO</td>
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<td></td>
<td>Corundum + Mica</td>
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</tbody>
</table>
- 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.