

**PARTICOAT**  
**Final Report**  
**DECHEMA-Forschungsinstitut (DFI)**

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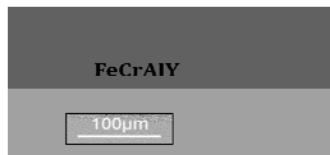
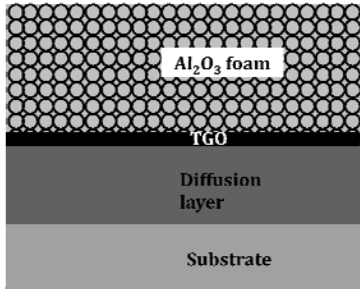
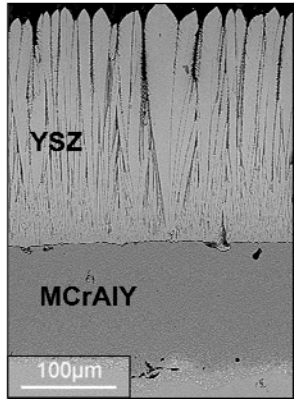
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**Sub project 1:**

**Work package 2:** Coating design for high temperature protection

The main objective of this work package is to create coating designs with regard to the selected applications for high temperature protection. DFI has contributed with different coating designs developments and tests to verify the viability of such designs.

Tested coatings differed basically in chemical composition and/or structure (see fig. 1). The chemical composition of the powder used to produce coatings ranged from pure aluminium based coatings, aluminium alloy based coatings (aluminium-silicon alloy) and composite cermet based coatings (aluminium mixed with magnesia, yttria stabilized zirconia or alumina). The coating structure was modified by grading the used particles size within the coating (from fine till coarse) or by adding different coating thicknesses in order to verify the particle size influence on the coating adherence.

State of the art coating		Particoat concept coating	
Description	Design	Description	Design
Diffusion layers produced on iron base alloys (ferritic or austenitic) by CVD or slurry route		Diffusion layer and top coat produced in a single step by slurry route.	
Diffusion layers produced on nickel base alloys by CVD or overlay coating techniques (HVOF,...). Top coats produced by PVD or APS			Al overaluminizing on standard MCrAlY
			Alumina top coat on standard TBC system

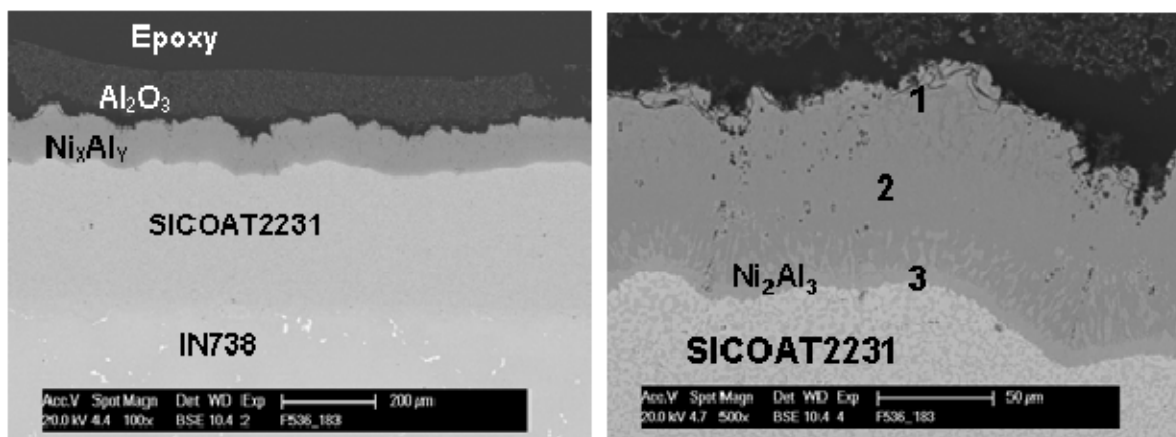
**Fig. 1:** Comparison of the state of the art coatings with the PARTICOAT design coating

The application of Al oxide quasi-foam structure developed within the PARTICOAT project will serve to increase the life-time of actual gas turbine blades for both, power generation as well as aero engines. The coatings based on an Al-slurry precursor could be deposited on three different surfaces; either directly on the substrate (nickel or iron base alloy), on the bond coat or on the thermal barrier coating (TBC)-top layer.

The first design aims to replace the standard TBC system coatings by the PARTICOAT design consisting of a diffused aluminium bond coat and hollow alumina spheres top coat.

Therefore, the aluminium based slurry precursor could be directly coated onto the substrate alloys of actual gas turbine blades for both power generation and aero engines.

The next design consisted in overaluminizing the standard bond coat by using PARTICOAT manufactured powder sources (see fig. 2). The use of the PARTICOAT manufactured powder source could eventually also serve to produce an aluminium oxide quasi-foam structure onto the standard overaluminized bond-coat. Consequently this system could also replace the standard TBC system coatings. However, the industrial partner's main request is the overaluminizing application. A very homogeneous diffusion layer was obtained between the SICOAT2231 and the layer made out of alumina hollow spheres. The obtained overaluminized zone has a thickness of approximately 80  $\mu\text{m}$ . The diffusion layer has a high aluminium content, typical for high activity pack aluminization.



**Fig. 2:** SEM cross-section of a PARTICOAT overaluminized state of the art overlay deposited MCrAlY coating.

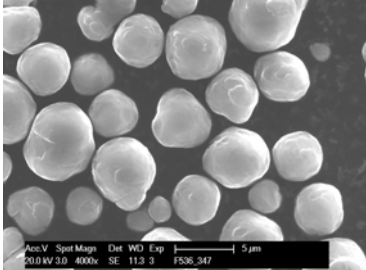
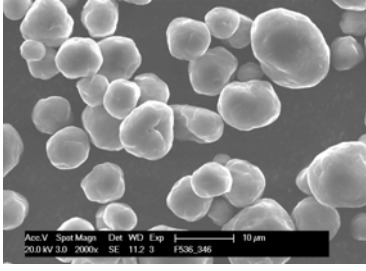
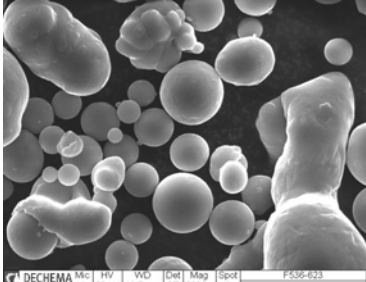
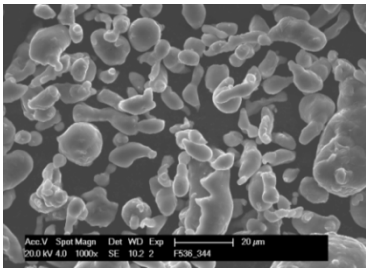
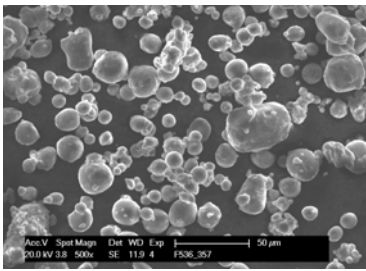
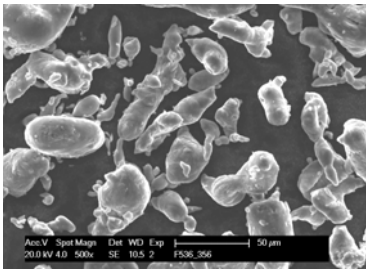
Finally the last design consists of protecting a standard ceramic thermal barrier coating actually used on power generation gas turbine blades by an Al-oxide quasi-foam. The main objective of such coating is to increase the stability of the standard Ytria Partially Stabilized Zirconia (YPSZ) when exposed to corrosive and erosive salts as CMAS.

The aluminium source material to produce the targeted coating designs will be described in WP3. The formulation of the different slurry compositions and the heat treatments needed to produce the targeted coatings will be studied in work-package 4. To test the coatings, complete characterization and life-time estimation will be carried out in work package 5. The alumina coatings produced by the PARTICOAT approach will be compared with coatings produced by pack cementation for comparison with the industrial specifications.

### **Work package 3: Source materials production**

DFI has identified European based suppliers of aluminium and aluminium alloy powder. These powders will be tested during WP4 and compared with the powders produced by Sibthermochem. Spherical aluminium powders have been obtained from MMG Aluminium Aktiengesellschaft (Mayen, Germany). The requested spherical aluminium has a high purity (contains less than 15 ppm Fe) and 0.4 % oxygen as maximum. Spherical aluminium and aluminium-silicon eutectic powders have been obtained from Poudres Hermillon (Hermillon, France).

The powder shape is shown in fig.3:

Source	Producer	Code	Particle size/ $\mu\text{m}$	spherical	figure
Al	Sibthermochim	0811-19	2-3	Yes	
		0911-35	20	Yes	
	MMG Aluminium Aktiegeshellshaft	MMG	10-20	Yes	
		Alpate	15-50	No	
	Aluminium Hermillon		20-50	Yes	
Al-Si			30-50	No	

**Fig. 3:** SEM pictures of DECHEMA-Forschungsinstitut tested aluminium source particles.

#### Work package 4: Coating manufacturing procedure

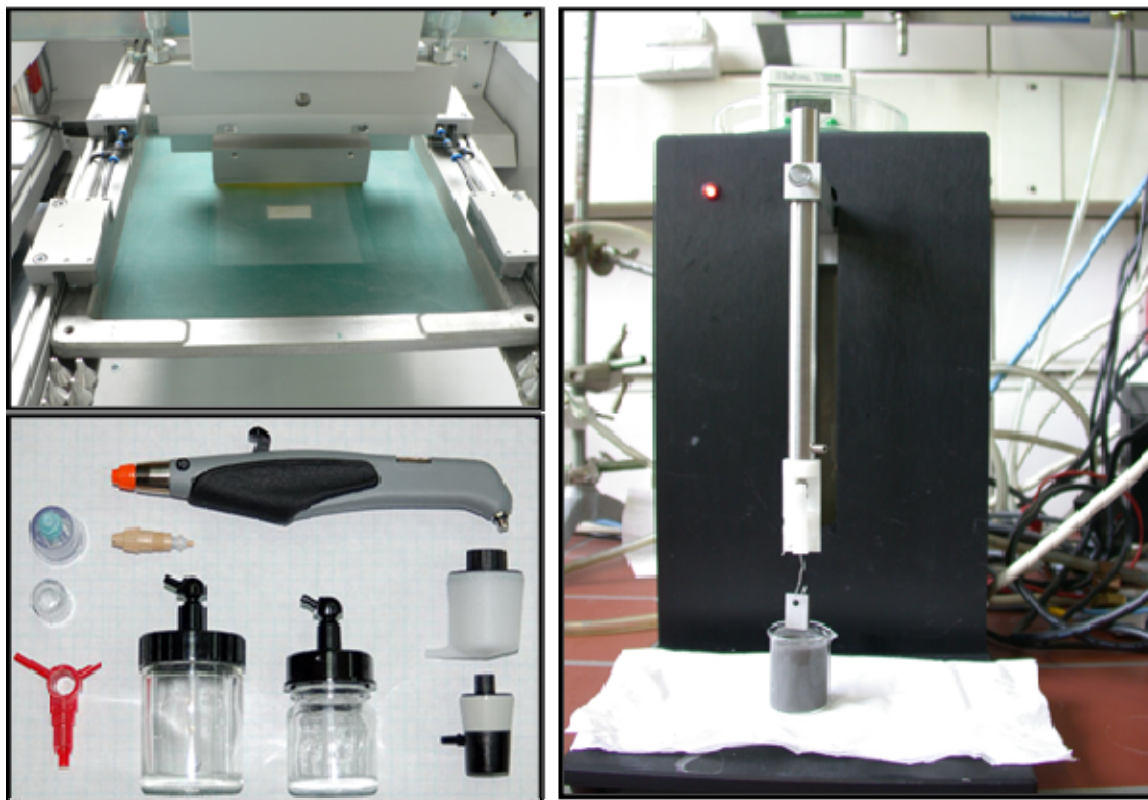
As described during work packet 2, DFI is involved in the development of the PARTICOAT concept onto different iron and nickel based alloy substrates. Different tasks have been carried out

- Selection of the coating technique (see fig. 4)
- Development of a slurry composition for each coating technique
- Selection of a powder source or combination to produce different coating structures
- Development of adequate heat treatments for each substrate
- Investigations to describe the coating formation mechanisms

DFI has finally provided R-Tech the information about the coating parameters in order to perform the risk assessment.

#### *Coating technique*

At first, the screen-printing method has been investigated. This method could only be applied to plane samples; therefore its applicability is restricted to the laboratory scale. However, due to the thickness homogeneity and reproducibility that this technique possesses the influence of different parameters during the study of the heat treatment procedure can be more accurately studied. A specific coating thickness can be easily obtained just by changing the used mesh. The mesh gives moist coating thickness before drying, which together with the slurry composition controls the final thickness of the coating after the sintering process.



**Fig. 4:** Screen-printer (top left) air brush (bottom left) and dip-coater (right) used at DECHEMA-Forschungsinstitut to produce coatings of sub-project 1.

Dip-coating has also been investigated as coating method for the PARTICOAT application. This method is highly interesting due to its potential to coat complicated shaped samples by a simple way. However, the rheological characteristics of the slurries needed for this method, only allow the deposition of thin layers (less than 20  $\mu\text{m}$ ) per processing step. The desired PARTICOAT ceramic top coat should range between 50 and 200 microns.

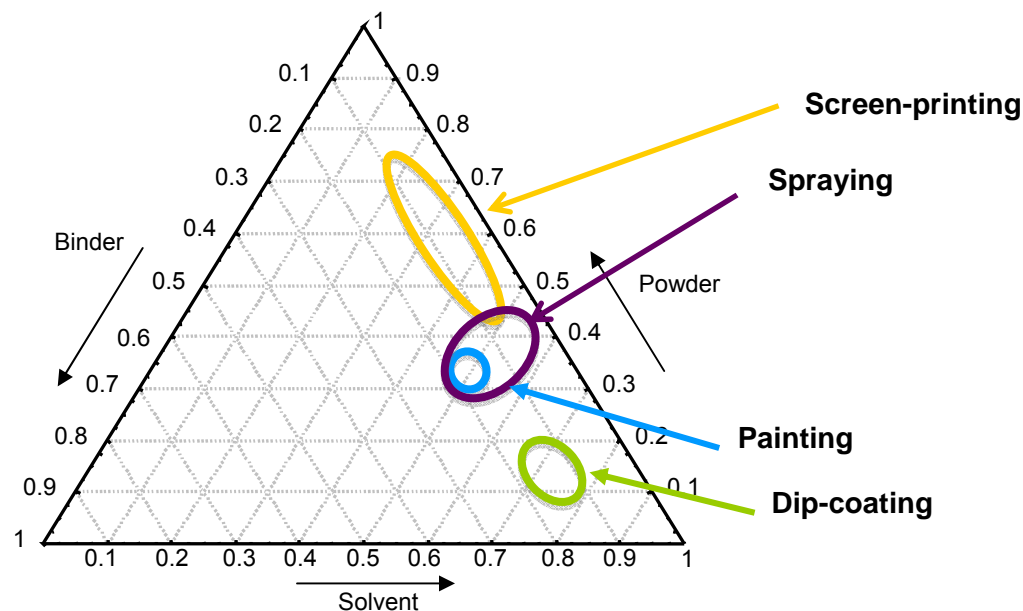
Coatings have been successfully deposited by air brush at DFI. This method is also highly interesting due to its flexibility. It allows the deposition of complex three dimensional shapes, which makes this method interesting for industrial applicability. The main problem of this method is the amount of slurry (or powder) that is wasted in every coating.

Painting as a coating method was also investigated at DFI. This method is very interesting due to its simplicity and easy industrial scale up for complicated three dimensional samples. In comparison to the air brush, no powder waste is produced by this method and no experienced technical workers are needed for its application, which makes this method a highly interesting coating method. The main problem of the method is the low reproducibility.

### Slurry composition

DECHEMA-Forschungsinstitut made a big effort in developing slurries. A large amount of coating methods were tested and rheological properties have to be adapted. For each process DFI investigated several slurries and tested different binders systematically, until the most adequate balance between the powder, binder and solvent type and quantity was obtained (see fig. 5).

The slurries developed for the screen-printing process need a high viscosity and could contain high powder quantities. The use of water as solvent is detrimental for those properties. The selected solvent and binder are terpeneol and ethylcellulose. After deposition of these slurries, the coated sample has to be dried in a furnace for at least 10 hours at 80°C. The binder evaporates at approximately 250 °C (measured at UC3M). As shown in figure 5 the slurries formulated for the screen-printing process contain a high amount of powder in comparison with the other slurries. Additionally, the slurries have been stored after use in a fume for more than six months and still showed enough stability for being used again.



**Fig. 5:** Ternary diagram of the slurry compositions developed at DECHEMA-Forschungsinstitut.

Different compositions have been tested for obtaining dip-coating slurries. All of them were water based slurries with different ranges of polyvinyl alcohol (binder) and aluminium powder. The main problem observed for these slurries was the long-term storage because

on the one hand, the aluminium was easily passivated within this solvent and on the other the solids of the slurry sediment, producing segregated phases. That consequently accelerated the evaporation of the water contained in the slurry. For avoiding some of the mentioned problems DFI tested the addition of polyacrylic acid and antifoam. These additives modified the viscosity of the slurry; therefore, further tests had to be carried out to adjust the optimal binder content of the slurry. These slurries ensured a quick drying process of about 1 hour, even at room temperature.

DFI developed slurries for deposition by painting. The selected solvent was ethanol to obtain a quick drying coating. In this case the tested binder has been polyvinyl butiral, additionally polyethyleneglycol was added as a plasticizer. The obtained slurry has shown a quick drying and soft structure, that allows a fast deposition of thick aluminium layers. The binder evaporation begins approximately at 300°C (measured at UC3M).

DFI together with Universite La Rochelle selected a binder and a slurry composition in order to produce slurries with adequate viscosity, drying velocity and coating rate to be deposited by air brush. The developed water based slurry contained polyvinylalcohol as binder and aluminium source powder. No harmful neither toxic elements as chromates or halide activators were introduced in the slurry. The same slurry composition can be used to coat different substrates with composition (iron base or nickel based alloys). For obtaining different coating thicknesses only the amount of the deposited slurry should be modified. As the air-brush technique is highly interesting for the industrial applications, the coatings to be tested in WP5 were entirely produced by this technique and slurry composition.

#### *Selection of powder source*

During work package 4 many parameters were systematically studied at DFI to obtain the coating design described in figure 1. After selection of the coating technique and slurry composition, different tests have been carried out in order to modify the resulting coating composition and structure. This involved changes mainly in the powder mixture or additions in the slurry to control the activity of the aluminium as summarized in the table 1. Different aluminium particle sizes have been studied. Cracks and adherence loss have been detected when using small particle sizes onto nickel and iron base alloys due to a large CTE mismatch between top coat and substrate induced by sintering of the top coat. Tests of slurries with different ranges of mixtures of aluminium and ceramics as magnesia or yttria have been done with the aim to improve the mechanical properties of the coating. Interestingly, these CERMET coatings did not hinder the formation of the diffusion layer. Some tests were also carried out by mixing halogen activators in different forms in the slurry in order to modify the activity of the produced slurries.

**Table 1:** Summary of slurry modifications examined to obtain the coating designs developed at DFI.

Substrate pre-treatment	Powder	Powder size
Ni plating AlCl <sub>3</sub> HF RE-sputtering	Al	31%0-5µm,69%5-10µm
	Al-Si	58%0.5µm,38%5-10µm,4%10-20µm
	Al+MgO	5.27µm-25.77µm/ D(4,3):12.34µm
	Al+YSZ	2.28µm-13.38µm/ D(4,3):6.01µm
	Al+Al <sub>2</sub> O <sub>3</sub>	2-3 µm
		5 µm
		20 µm
		20-50 µm

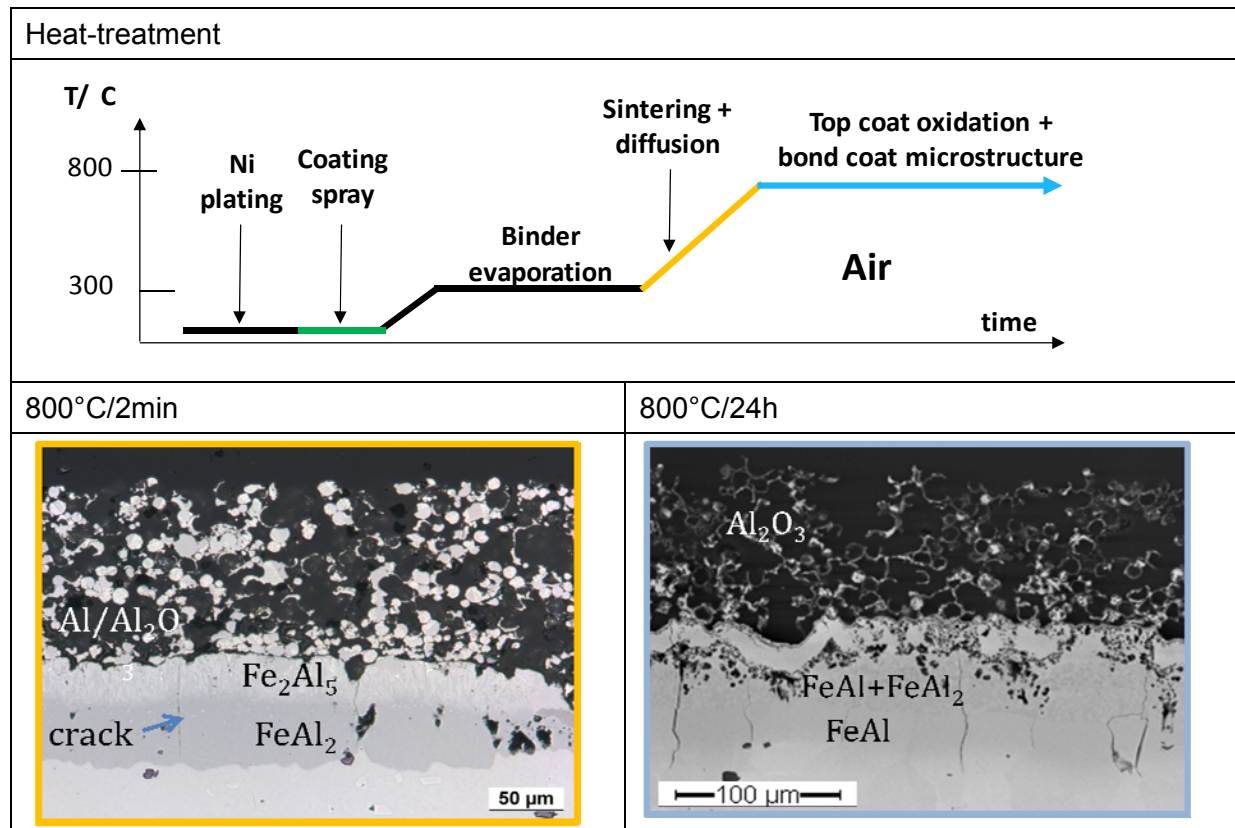
#### *Heat treatment*

DFI has developed a systematic screening of different parameters to obtain adherent coating systems. Matrix parameters have been the substrate type, the powder size (and batch), the slurry composition (and deposition method), the exposure atmosphere as well as the duration temperature and temperature steps and ramps of the thermal treatment.

A heat treatment was developed for iron base alloys in order to produce an alumina foam top coat and aluminium rich diffusion layer at low temperatures in order to maintain the

mechanical properties of the substrate. Thermal treatments were developed in inert atmospheres as Ar/H<sub>2</sub>(5%), Ar or even H<sub>2</sub> and in air. However, due to the searched top coat stability and the industrial interest on using the slurry coatings as a repairing method, the coatings tested in WP5 were entirely produced in air.

The parameters required to produce the coatings onto iron base alloys by using a reproducible method and the resulting cross-sections are summarized figure 6.

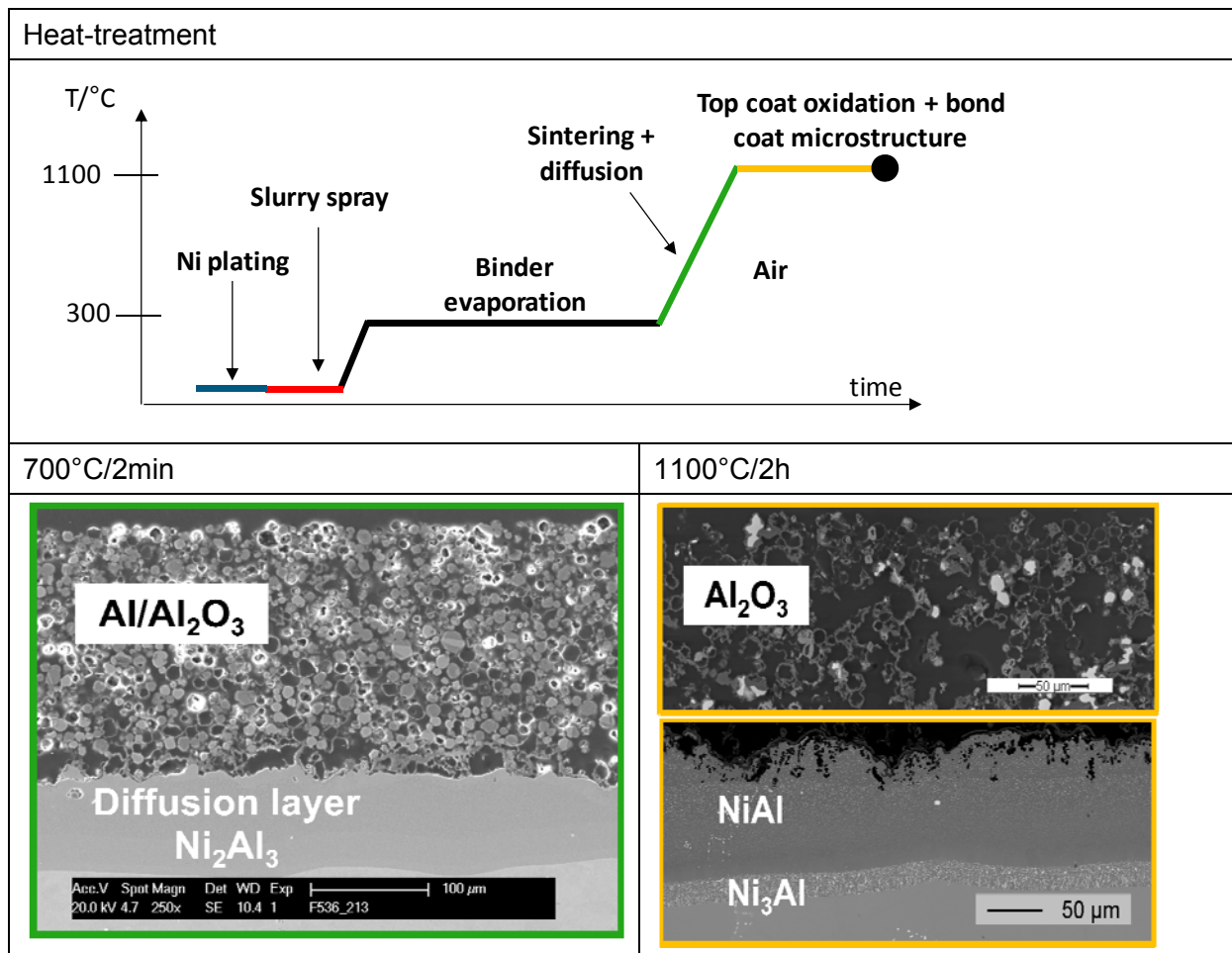


**Fig. 6:** Coating deposition and heat treatment procedure developed at DECHEMA-Forschungsinstitut for iron base alloys (top). SEM cross-sections of the coating during the sintering step (bottom left) and after finishing the heat-treatment (bottom right).

The coating, consisting of hollow alumina spheres shows a thickness of approximately 100 µm and a diffusion layer of approx. 75 µm.

A heat treatment was developed also to produce diffusion layers for nickel based superalloys with adequate phase and microstructure. The effect of particle size, composition and form effect was verified as well. Following a similar experimental matrix, the parameters required to produce the coatings onto nickel base alloys by using a reproducible method were selected and are summarized in figure 7.





**Fig. 7:** Coating deposition and heat treatment procedure developed at DECHEMA-Forschungsinstitut for nickel base alloys (top). SEM cross-sections of the coating during the sintering step (bottom left) and after finishing the heat-treatment (bottom right).

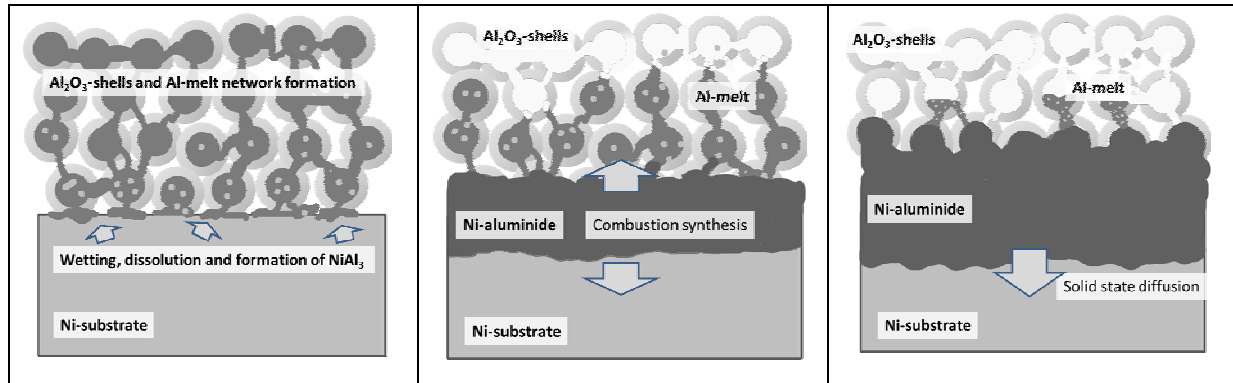
Light microscopy cross-sections are shown in figure 7. The obtained layer build of alumina hollow spheres quasi foam top layer is approximately 200  $\mu\text{m}$  thick and shows very good adherence. A very homogeneous diffusion layer was obtained between the substrate and the alumina hollow spheres with a thickness of approx. 100  $\mu\text{m}$ .

These model coatings are tested during work package 5 and compared to standard industrially based coatings for different kinds of applications as thermal barrier coatings in aeronautical or energy industries and heat exchangers in waste incineration. It is important to remember that the work package 4 is a product of the iteration carried out for improving the coating designs described within the work package 2 together with the results obtained during work package 5, therefore it has been highly time consuming and needed special attention.

#### *Hollow spheres formation and mechanism to form PARTICOAT coatings*

The mechanism for the aluminium to get in contact with the iron or nickel base substrate and the reaction to produce the diffusion layer were investigated by DFI researchers (see fig. 8). As a short description of the coating formation can be explained by the fact that for aluminium spherical particles at temperatures below the melting point of aluminium, oxidation proceeds slowly due to the diffusion of oxygen through the oxide shell. Upon melting of aluminium, the density of aluminium changes, resulting in a volume expansion, however, the solid oxide shell cannot follow this expansion which causes the oxide shell to be in tension

and the aluminium metal core to be in compression. The pressure gradient present inside the particle can result in rupture of the oxide shell and thereby making Al available at the surface of the shells by its penetration through cracks. The molten aluminium itself forms a network in its oxide shells, favouring the wetting of nickel or iron with aluminium melt. In such way large amounts of aluminium become available from the aluminium spheres to get in contact with the metal of the substrate.



**Fig. 8:** Schematics describing the mechanism to produce PARTICOAT coatings on metallic substrates.

The diffusion layer formation is controlled by three steps: Al close to the melting point **dissolves** nickel or iron from the surface and changes into the molten state. At the initial moment of reaction, the produced composition is eutectic. In the process of dissolution the average concentration of nickel or iron in the diffusion layer increases. At the inter-phase a saturated molten layer must exist, that wets the substrate and determines the rate of movement of the atoms of the solid nickel or iron into that of the molten aluminium. Because in the binary (Ni-Fe)Al-system there are intermetallic compounds, simultaneously with the dissolution of nickel or iron, the formation of an intermetallic layer at the interface is the consequence. The aluminides are formed by an exothermic reaction, which continuously proceeds. The exothermic reactions of dissolution and local formation of the aluminium rich (Ni-Fe)Al phase increase the temperature; this increase leads to further dissolution of nickel or iron and the further formation of more (Ni-Fe) rich intermetallic phase. This step is controlled by a **combustion synthesis** steadily rising the temperature and finishes when the melting and dissolution decreases in favour of the formation of intermetallics. After the combustion reaction the diffusion in the system is controlled by **solid state inter-diffusion**, which is, compared to combustion synthesis, an extremely slow process.

### Work package 5: Performance and degradation mechanisms

DECHEMA-Forschungsinstitut has been working intensively on work-package 5, "Performance and degradation mechanisms". The work carried out can be summarized as follows:

- Short and middle term (100-3000 hours) exposure under oxidative or corrosive environments (**chlorine, air and sulphidation**) of PARTICOAT coated iron and nickel base alloys.
- Microstructural and mechanical characterization of the coatings in order to obtain a satisfactory model to assess the lifetime of the PARTICOAT designed coatings in comparison to the WP1 selected state of the art coatings.
- Evaluation of the thermal barrier effect of the produced coatings
- Simulation of the top coat crack propagation

## Work package 5.1: Oxidation, corrosion and diffusion processes

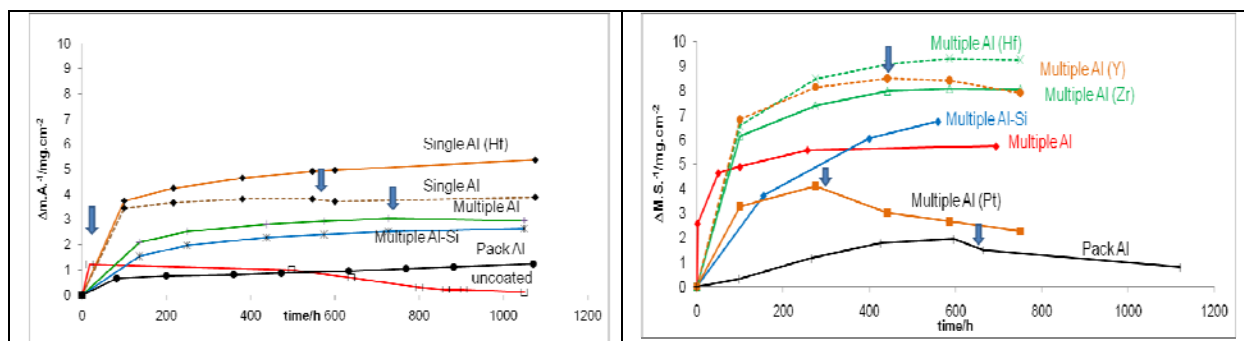
DFI has investigated the oxidation, corrosion and diffusion processes of nickel and iron based alloys coated with aluminium and aluminium-silicon alloy powder sources. The tests were carried out as summarized in table 2.

**Table 2:** Summary of oxidation and corrosion tests carried out at DECHEMA-Forschungsinstitut for iron and nickel base alloys coated with PARTICOAT

Substrate	Tested coating	Experimental conditions	Characterization
<b>CM247</b> (Ni-base)	Al Al-Si	1100°C Air	LOM XRD TGA SEM ESMA
		1000°C Air 1000°C SO <sub>2</sub> (Synthetic air+1.5 SO <sub>2</sub> vol.%)	
<b>AISI446</b> (High Cr ferritic) <b>AISI347</b> (Middle Cr Austenitic) <b>P91</b> (Low Cr ferritic-martensitic)	Al Al-Si	800°C Air 800°C Cl <sub>2</sub> (Synthetic air+4.9Ar+0.1Cl <sub>2</sub> vol.%)	
		600°C Air 600°C Cl <sub>2</sub> (Synthetic air+4.9Ar+0.1Cl <sub>2</sub> vol.%)	

### Oxidation at 1000°C and 1100°C of PARTICOAT coated nickel base superalloy

This series of tests was carried out in order to select the appropriate particle size, composition and possible substrate pre-treatment to obtain an adherent top coat and homogeneous diffusion layer onto nickel base alloys for aero-engine application. The Al slurry produced coatings are compared with reactive elements modified diffusion coatings and high activity pack cemented diffusion coatings. Figure 9 represents the mass evolution of the tested coatings on CM247.



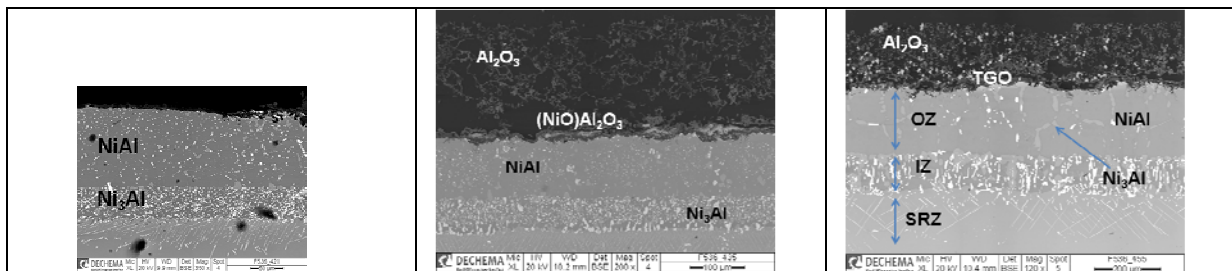
**Fig. 9:** Weight evolution curves of CM 247 nickel base alloy PARTICOAT coated samples in air at 1000°C (left) and 1100°C (right).

At 1000°C the slurry based coatings show higher weight gain in comparison to the uncoated or pack aluminizing coated. For the slurry produced coatings weight gain is concentrated in the beginning of exposure (during the first 100 hours) and after this period the weight increases steadily for both coatings, being more pronounced for the Hf doped coating. Among the slurry produced coatings, the ones with smaller particle size show the highest

weight gain, due to the biggest active area to be oxidized. For the uncoated CM247 spallation after 20 hours of exposure occurred.

At 1100°C, tendencies are similar, showing the lowest weight gain for the pack cemented case. Different reactive element modifications have shown to be detrimental for the weight gain, even if the top coat showed improved adherence. The case of the Al-Si based coating has shown a detrimental effect at temperatures above 1100°C due to the formation of mullite (not observed at 1000°C).

The cross section of the multiple Al size produced coatings after exposure at 1000°C are compared with the high activity pack aluminized ones in figure 10. The microstructure and the composition of both produced coatings are very similar. The main difference between these two coatings is the top coat on the PARTICOAT coatings, which has the potential to serve as a thermal barrier coating.



**Fig.10:** SEM cross-section of CM247 pack cemented (left) and multiple Al sized powder PARTICOAT coated (centre) exposed for 1057 hours in 1000°C and multiple Al sized powder PARTICOAT coated exposed for 750 hours in 1100°C.

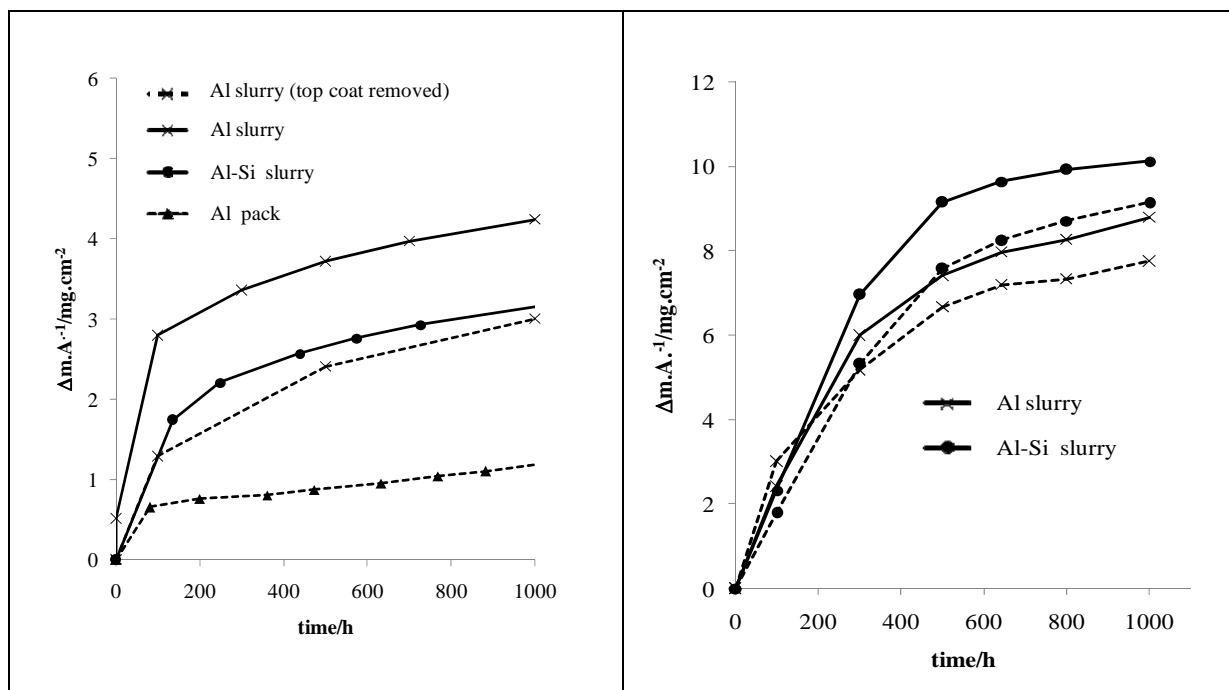
The adherence of the multiple Al size produced top coat is not affected after 750 hours of exposure at 1100°C (see figure 10, right). The effect of the temperature increase is mainly accompanied by aluminium depletion at the grain boundaries of the diffusion layer.

The most important findings could be summarized as following:

- The largest mass gain is observed for the slurry produced coatings. It is related to the coating formation and the large oxidative surface that the micron sized particle source have in comparison to the pack cemented or uncoated surfaces.
- After the formation of the coating (total oxidation of the top coat), the mass gain is related to the oxidation of the diffusion zone, which consists of different  $Ni_xAl_y$  phases.
- The initial weight gain increases by decreasing the source particle size.
- The increase of source particle size has improved the adherence of the top coat.
- The addition of reactive elements has improved the adherence of the top coat.
- The most promising coatings were produced by using multiple Al and Al-Si particle sized metallic powders
- The use of Al-Si as source particle is detrimental for temperatures above 1000°C
- The coatings have been successfully produced on commercial alloys by air brush and heat treatments in air.

#### *Oxidation and sulphidation of PARTICOAT coated nickel base superalloy*

The next series of experiments were carried out in order to verify the protection of the previously selected most promising coatings against sulphidation. Figure 11 represents the mass gain evolution of CM247 coated by an Al and Al-Si alloy powder, deposited by air brush after exposure at 1000°C in air and SO<sub>2</sub> containing oxidizing atmosphere.



**Fig. 11:** Weight gain curves of CM 247 coated by pack and slurry exposed at 1000°C in air for up to 1000 hours (left). Weight gain curves of CM 247 coated by slurry exposed at 1000°C in 1.5 vol. % SO<sub>2</sub> containing synthetic air for up to 1000 hours (right). Continuous line represents the systems with diffusion layer and top coat and the dashed lines systems based only in diffusion layer.

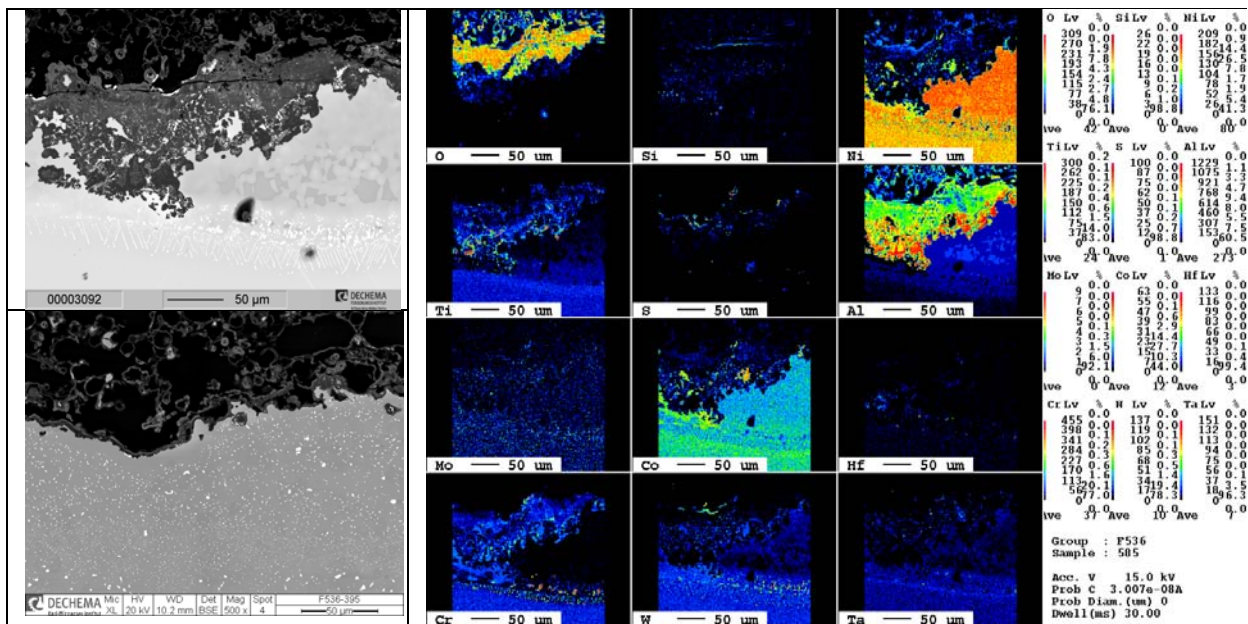
For exposures in air, aluminium pack cemented coating shows the lowest weight gain after 1000 hours of exposure, followed by slurry coated aluminium without top coat. The highest weight gain is observed for the Al slurry coated sample with top coat, while the Al-Si slurry coated sample with top coat is found between the two Al slurry produced coatings. It is easily observed that the main weight change of the slurry coated samples with top coat is observed during the first 100 hours of exposure, this weight gain is related to the oxidation and formation of the top coat oxide foam, the case of the Al-Si coated slurry shows lower initial weight gain because of the higher particle size of the used metallic particles, which influence the effective area to be oxidized. After this period the weight gain increases in a similar way for all the coatings.

The weight gain of the coatings after exposure in SO<sub>2</sub> containing oxidizing atmosphere is shown in figure 11, on the right side. In this case, the aluminium pack cemented is not included due to the similarities in the diffusion layer microstructure with the aluminium slurry produced coatings. For this atmosphere the comparison was done between slurry coatings with and without the top coat. Samples with top coat show higher weight gain than those without top coat. This is due to the important area that represents the top coat transformation of aluminium based particles to the alumina based foams during exposure. Al-Si slurry produced coatings show lower weight gains than those of Al during the first 300 hours of measurement (in accordance with the test in air) and show the highest weight gains after 1000 hours of exposure. In contrast to the exposures in air, where the weight gain of the slurry coatings was concentrated in the first 100 hours of exposure, for the SO<sub>2</sub> exposed samples the weight gain increases markedly during the first 500 hours and stabilizes later, independently of if the sample has or has not a top coat. Therefore this acceleration in the growth rate is believed to be related to the exposure atmosphere.

Effectively, the SEM cross-section of the Al slurry coated CM 247 after 500 hours (figure 12) shows an extended typical type I hot corrosion attack related to sulphidation/oxidation in the diffusion layer for SO<sub>2</sub> containing atmosphere. A close investigation of the diffusion layer and the element mapping for the sulphidizing atmosphere is shown in figure 2b. The diffusion layer is attacked in depth, forming mainly alumina, but a better observation of the element mapping reveals sulphur enrichment between the newly transformed diffusion layer and the

unaffected diffusion layer. Thus, the primary mode of attack seems to be internal sulphidation/oxidation. This attack has been previously observed during high temperature exposure in an oxidizing/sulphidizing gas mixture and can be explained in the following manner. The surface scale formed on the diffusion layer was not completely protective, and internal precipitates of  $Al_2O_3$  began to form as oxygen dissolved into and diffused through the alloy. Sulphur also dissolved and diffused into the alloy; however, since  $Al_2O_3$  is much more stable than  $Al_2S_3$ , only the oxide was observed in the upper regions of the internal precipitation zone. Specifically, the solubility product for  $Al_2S_3$  formation could not be exceeded in the internal oxidation zone near the alloy surface. Accordingly, sulphur continued to diffuse through this internal oxidation zone until it reached a point where the oxygen activity was low and the sulphur activity was sufficiently high to produce sulphides from the aluminide. At this location, internal  $Al_2S_3$  began to precipitate. As oxygen continued to arrive at the  $Al_2O_3/Al_2S_3$  interface, the oxygen activity increased and consequently the sulphide at this interface was converted into oxide. As a result of this conversion, sulphur was released and diffused further into the alloy to form more sulphides a deeper internal sulphidation zone. As direct consequence of the described sulphidation/oxidation, accelerated aluminium depletion occurs in comparison to the exposures in air. This can be easily observed comparing figure 12, where in the case of the exposure in sulphidizing/oxidizing atmosphere after 500 hours very few NiAl is present while in the case of exposure in air no depletion of NiAl has been observed. Similar effects have been observed for the case of the Al-Si slurry produced coatings.

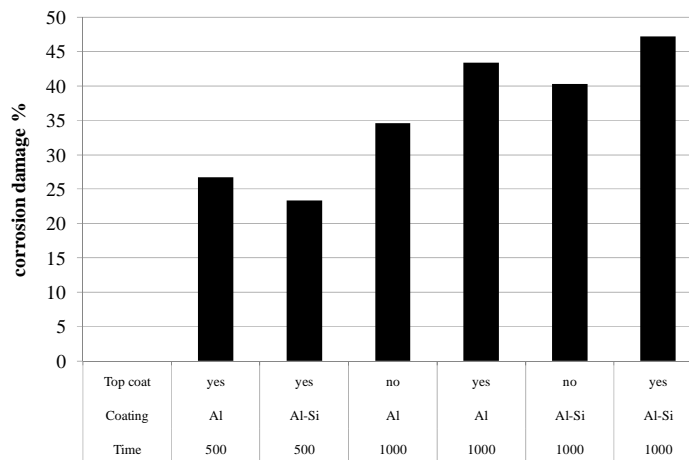
It has also been observed, that the top coat provokes rumpling of the diffusion layer as shown in figure 12. For the case of the pack cemented coating and for that of the PARTICOAT system with the removal of the top coat before exposure (without any top coat), no rumpling has been observed at the tested conditions.



**Fig. 12:** SEM cross-section of Al slurry coated CM 247 exposed at 1000°C for 500 hours in  $SO_2$  containing synthetic air (left, top) EPMA mapping of the latest (right) and SEM cross-section of the same coating when exposed to air (left, bottom).

The coating damage diagram, which represents the relative quantity of diffusion layer which has been affected by the sulphidation is shown in figure 13. It can be seen that at 500 hours of exposure under  $SO_2$  containing synthetic air atmosphere the oxidized/sulphidized damaged diffusion zone is slightly higher (around 25%) for Al than for the Al-Si slurry produced coating with a top coat. After 1000 hours of exposure these values increased for both coatings (ranging around 45%), but interestingly the damage values are inverted, with the Al-Si slurry based coating being more prone to attack. A similar inversion has been also

observed in the weight gain evolution as shown in figure 1. The comparison of the same slurry produced coatings without top coat show similar tendencies as those observed at 1000 hours of exposure; however, the damage quantity is lower than for the cases in which the top coat is present.



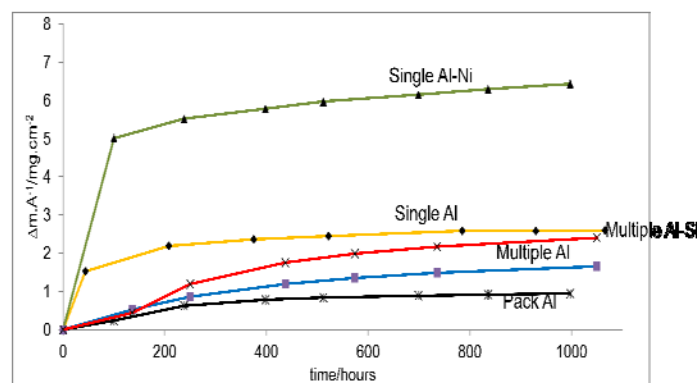
**Fig. 13:** Quantification of damaged diffusion layer obtained by image analysis of SEM cross-section of SO<sub>2</sub> containing synthetic air exposed CM 247 slurry coated samples at 1000°C.

The most important findings could be summarized as following:

- When exposed to sulphidizing/oxidizing atmosphere, the quantification of the damaged coating shows that silicon modified coatings behave better than simple aluminide slurry produced coatings while the silicon is maintained in the coating (the first 500 hours).
- Differently to the observations in air, when exposed to sulphidizing/oxidizing atmosphere, the alumina based top coat produces a negative effect, increasing the corrosion of the diffusion layer by producing a less protective oxide scale probably due to the rumpling, which the alumina based top coat coatings undergo.

#### Oxidation of PARTICOAT coated iron base alloys at 800°C

This series of tests was carried out in order to select the appropriate particle size and composition to obtain an adherent top coat and homogeneous diffusion layer onto iron base alloys. Figure 14 represents the mass gain evolution of the ferritic AISI446 (high Cr content) coated by an Al and Al alloy powder, deposited by air brush after exposure at 800°C in air. These slurry produced coatings are also compared with high activity pack cemented coatings.

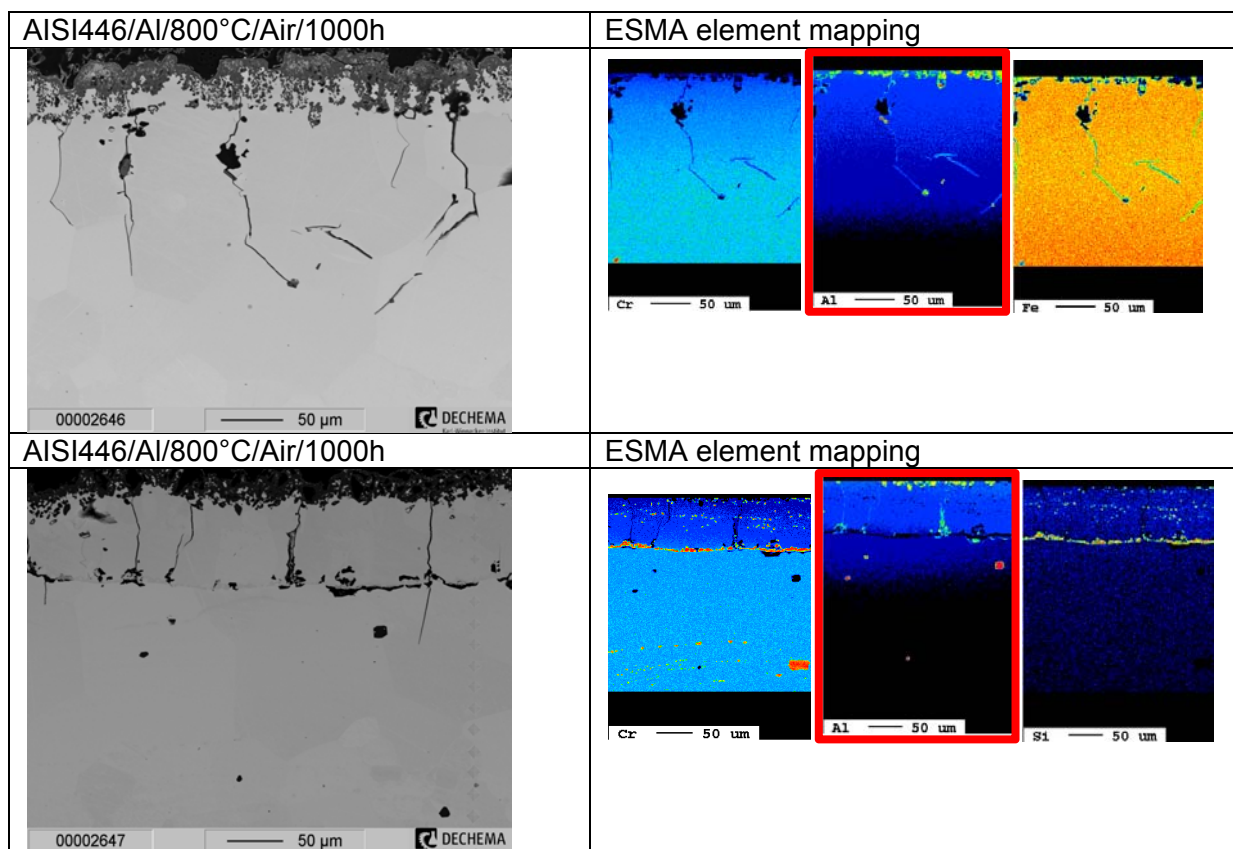


**Fig. 14:** Weight gain evolution of different Al and Al alloy powder coated AISI446 exposed in air for 1000h at 800°C

The most important findings could be summarized as following:

- The coatings have been successfully produced on commercial alloys by air brush and heat treatments in air.
- After the formation of the coating, the mass gain is related to the oxidation of the diffusion zone, which consists of different  $Fe_xAl_y$  phases.
- The initial weight gain increases by decreasing the source particle size.
- The increase of source particle size has improved the adherence of the top coat.
- The use of Al and Al-Si as source particle with sizes of more than  $20\ \mu m$  was further studied due to its improved top coat adherence and low oxidation rates.

These Al and Al-Si produced coatings showed important differences in the diffusion layer. For high chromium containing iron base alloys aluminium inter-diffusion from diffusion layer through the substrate decreased strongly, as observed in figure 15 elements mapping.



**Fig. 15:** SEM cross-section (left) and EPMA elements mapping (right) of Al (top) and Al-Si (bottom) slurry coated AISI446 after 1000 hours of exposure in air at 800°C.

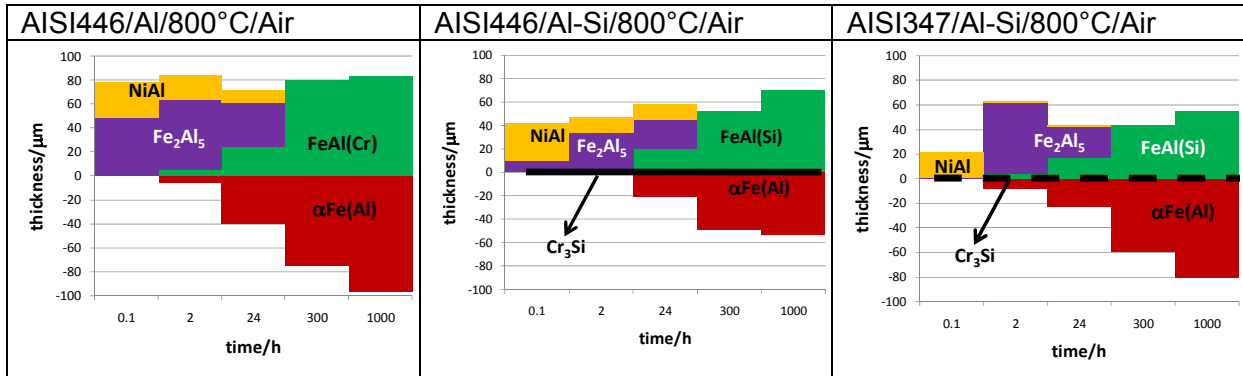
Image analysis of cross-sections of Al and Al-Si produced coatings from particles with more than  $20\ \mu m$  are summarized schematically in figure 16. These figures present mainly information about the diffusion layer thickness and composition (above 0 y axes) and inter-diffusion zone thickness (below 0 y axes) as a function of time.

The most important findings could be summarized as following:

- Aluminium based slurries produced thicker diffusion layers than Al-Si based ones
- At 800°C Al inter-diffusion increases strongly. This effect is detrimental due to the overall Al reservoir decrease in the coating, which reduces the coating life-time.



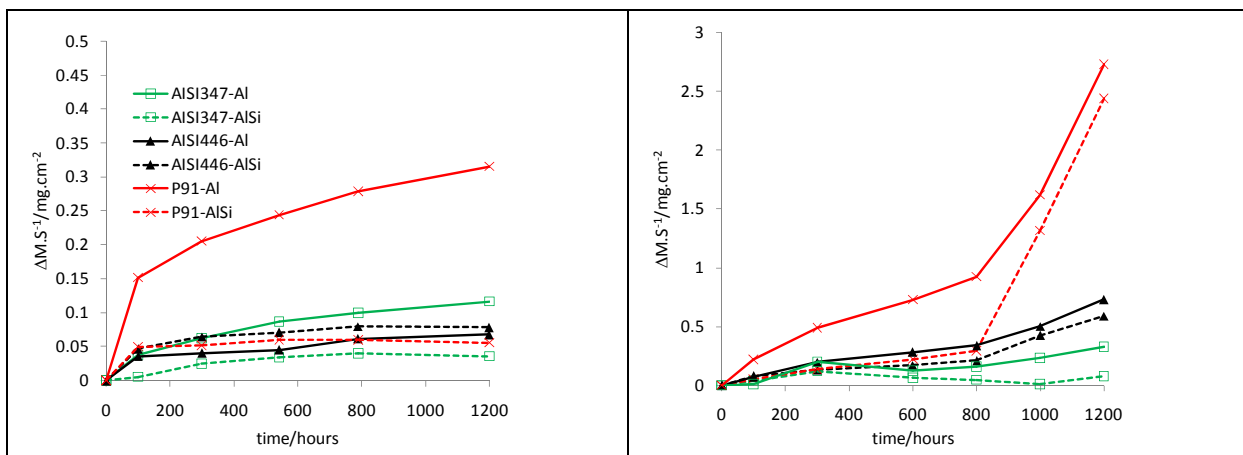
- For Al base coatings ferritic substrates show higher inter-diffusion than austenitic substrates.
- Si addition decreases inter-diffusion for high Cr content ferritic substrates due to formation of  $\text{Cr}_3\text{Si}$  between the diffusion and inter-diffusion layer.
- Si addition increases inter-diffusion for austenitic substrates due to the stabilization effect of the ferritic phase.



**Fig. 16:** Summary of diffusion layer phase thickness in function of time obtained after SEM cross-section analysis for different PARTICOAT coatings deposited onto iron base alloys after exposure in air at 800°C.

#### *Oxidation and chlorine/oxidizing atmosphere exposure of PARTICOAT coated iron base alloys at 600°C*

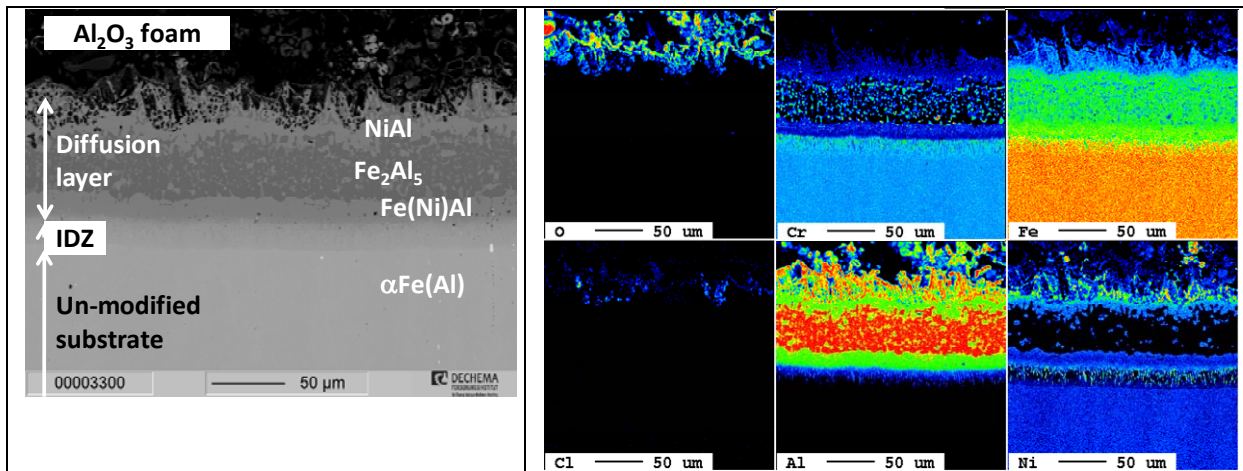
The weight gain evolution in air of Al and Al-Si slurry coated iron based alloys is shown in figure 17, left. Low Cr containing steel (P91) shows the highest weight gain, followed by high Cr containing alloy (AISI446). The lowest weight gain is measured for the austenite alloy (AISI347). Aluminium slurry produced coatings show higher weight gains than Al-Si produced ones. The chlorine containing oxidizing atmosphere exposure of the weight gain of the coating in  $\text{Cl}_2$  containing oxidizing atmosphere is shown in figure 17, right. The tendencies are similar as the described for exposures in air, however, the weight gains increased strongly, related to the “active oxidation” corrosion effect formed because of the exposure atmosphere. At the end of the exposure the weight gain increased dramatically due to the spallation of the coating in the corners of the samples, leading to an easier chlorine attack of the samples at such spots.



**Fig. 17:** Weight gain evolution of the coated alloys at 600°C in air and 0.1%  $\text{Cl}_2$  containing oxidizing atmosphere

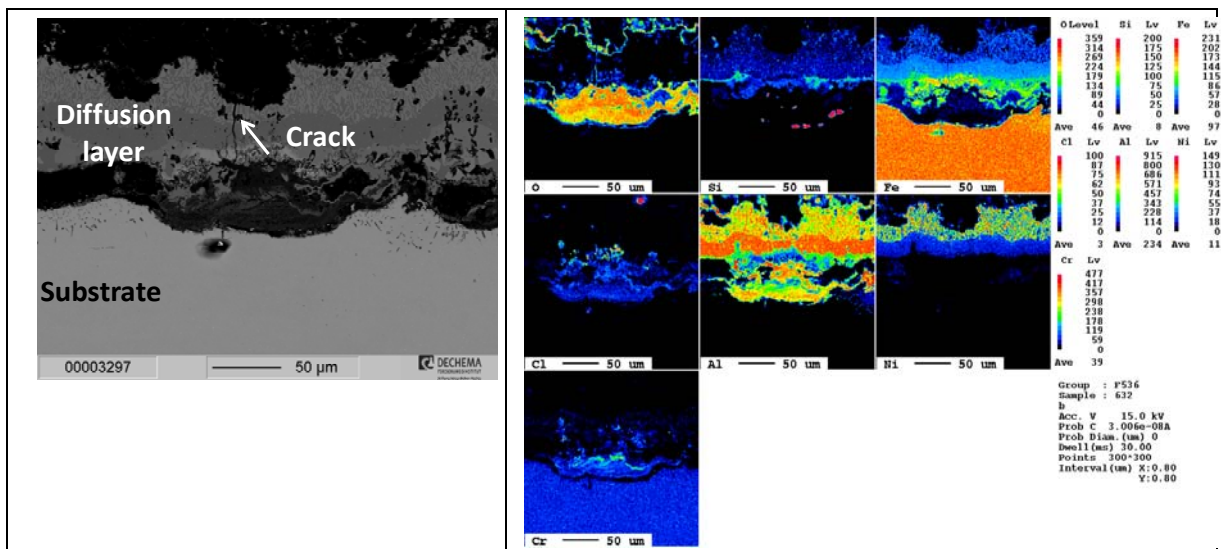
The cross section of the Al produced coatings on AISI347 after exposure in chlorine containing oxidizing atmosphere at 600°C is shown in figure 18. No chlorine species were

found in the diffusion layer. The diffusion layer consists of FeAl and NiAl, and no cracks were present.



**Fig. 18:** SEM cross-section of Al slurry coated AISI347 exposed at 600°C for 1200 hours in chlorine containing synthetic air (left) and EPMA element mapping (right).

The cross section of the Al produced coatings on P91 (9 at.% Cr) after exposure in chlorine containing oxidizing atmosphere at 600°C is shown in figure 19. Chlorine species were found in the diffusion layer. The diffusion layer consists on FeAl and NiAl cracks were present, allowing the easy penetration of chlorine species through the layer to the substrate. The same observations were made also with ferritic AISI446 (24 at.% Cr). However, due to the high chromium and silicium content of the diffusion layer, the chlorine attack was less pronounced than in the case of P91 steel.



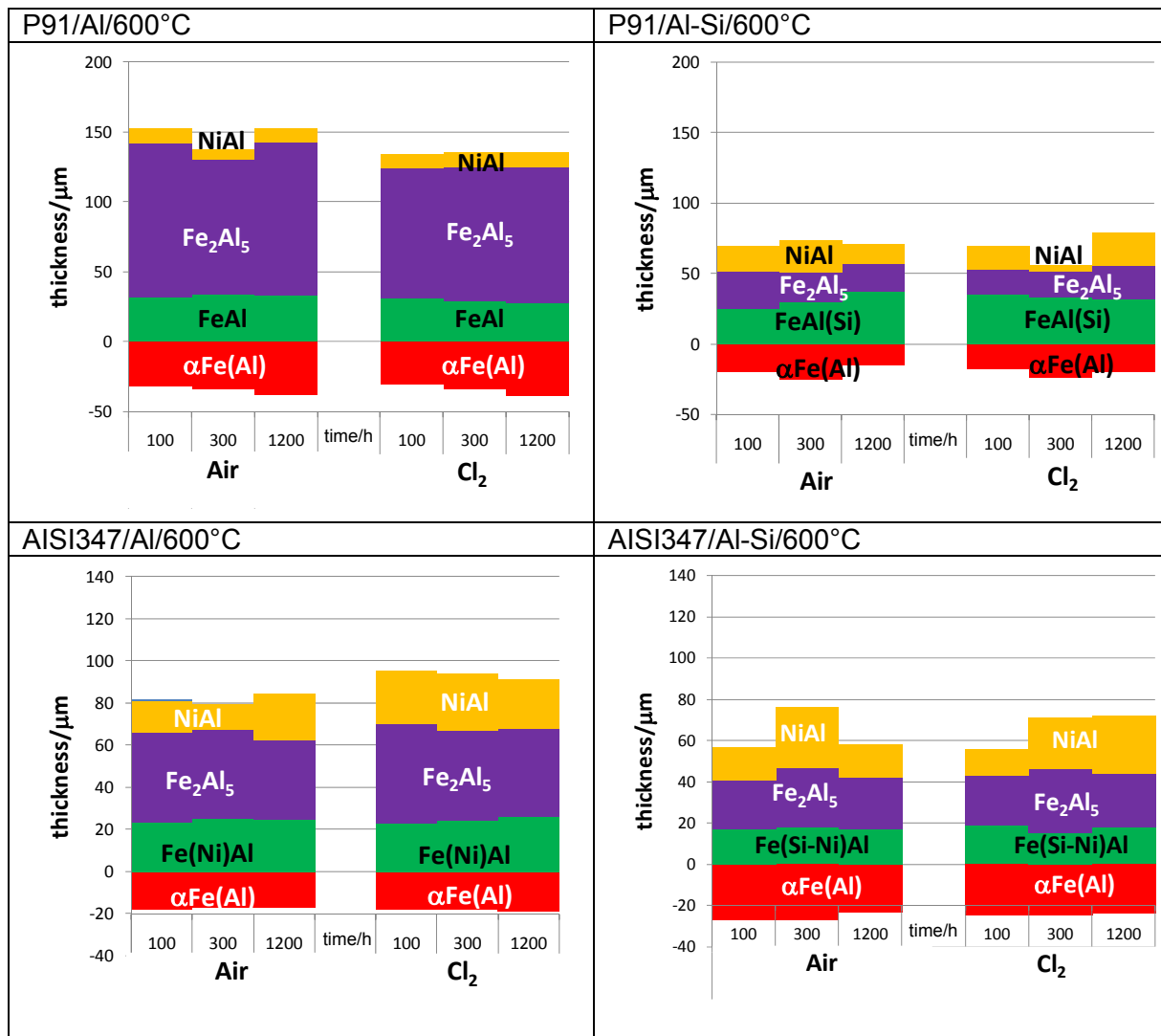
**Fig. 19:** SEM cross-section of Al slurry coated P91 exposed at 600°C for 1200 hours in chlorine containing synthetic air (left) and EPMA element mapping (right).

The most important findings could be summarized as following:

- The largest mass gain is observed for P91, followed by AISI446 and the lowest observed for AISI347
- Al slurry coatings produce higher weight gains than Al-Si produced ones
- The previous two observations are consistent in air and chlorine containing oxidizing atmosphere

- The use of Al-Si as source particle is beneficial in chlorine containing oxidizing atmospheres. The performance of such coatings improves by increasing the Cr content of the substrate.
- Cracks presented in diffusion layers of ferritic steels are detrimental during exposures in corrosive atmospheres due to easy penetration of corrosive species.

Image analysis of cross-sections of the Al and Al-Si produced coatings has revealed relevant information about the aluminium inter-diffusion and phase stability. Results are summarized schematically in figure 20. At 600°C the diffusion layer formed phases, contrarily to those observed at 800°C did not evolve as a function of time. They do not disappear or transform into lower Al containing phases. Aluminium diffusion through the inter-diffusion zone is strongly reduced (in comparison to the observations at 800°C). Therefore, it can be concluded that these coatings should possess no problems from an Al reservoir perspective at temperature ranges below 600°C. About the influence of the substrate composition, the observations made at 800°C are still applicable. It has to be remembered that these coatings have been produced at 800°C with a pre-treatment of 24 hours in air even if they are exposed at 600°C.



**Fig. 20:** Summary of diffusion layer phase thickness in function of time obtained after SEM cross-section analysis for different PARTICOAT coatings deposited onto iron base alloys after exposure in air and chlorine containing atmosphere at 600°C.

The findings can be summarized as follows:

- Aluminium based slurries produced thicker diffusion layers than Al-Si based ones
- For Al based coatings ferritic substrates show higher inter-diffusion than austenitic substrates.
- Si addition decreases inter-diffusion for AISI446 (high Cr content) ferritic substrates due to formation of a continuous  $\text{Cr}_3\text{Si}$  layer between the diffusion and inter-diffusion layer.
- The  $\text{Cr}_3\text{Si}$  layer is not continuous in the case of AISI347 nor is P91, therefore, the decrease of aluminium inter-diffusion was not so strong in these cases. The studies carried out were not enough to give an accurate value of the minimum Cr content of the substrate to perform such continuous layers, however, approximate values should range around 24 at. %.
- Si addition increases inter-diffusion for austenitic substrates due to the stabilizing effect on the ferritic phase.
- After 1000 h of exposure in air and  $\text{Cl}_2$  containing atmosphere of the aluminium content in the diffusion layer was maintained around 48 at.% for all the coatings. This value means almost no Al reservoir recession at 600°C.

## Work package 5.2: Mechanical properties

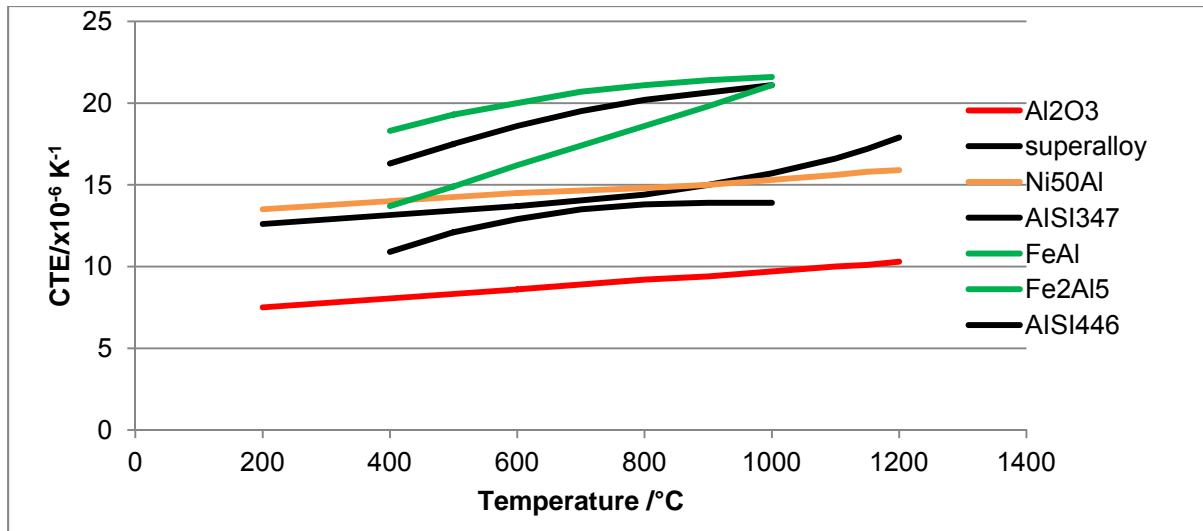
DECHEMA-Forschungsinstitut has studied the mechanical stability and adherence of the produced coatings. An interesting point of these new coating is that no previous information about the mechanical properties or how to analyze them is known due to its innovative form. Therefore, a trial of tests has been carried out and summarized in table 3.

**Table 3:** Summary of mechanical tests carried out at DFI for evaluating the developed PARTICOAT coating designs.

Tests	Aim of the study
Dilatometry	Top coat adherence influence on thermal expansion coefficient. Diffusion layer cracks influence on CTE
Nano-hardness	Diffusion layer hardness and Young modulus
Micro-hardness	Diffusion layer hardness
4PB coupled to Acoustic emission (AE)	Spallation of top coat
Isothermal and Cyclic oxidation coupled to AE	Crack propagation behaviour

### CTE

The thermal expansion coefficients mismatch is important in order to coat nickel or iron base alloys and was compared with published data. It has been demonstrated that the CTE mismatch between the top coat (alumina) and substrate was an important factor for coatings produced on nickel base alloys and austenite steels because it could induce top coat spallation. Top coat adherence decreased strongly with decreasing particle size. The CTE mismatch between the substrate and the diffusion layer (see fig. 21) is of strong importance for iron base ferritic steels, where due to a large mismatch vertical cracks are observed which could provoke easy paths for corrosive elements in the gas or liquid phase through substrates.



**Fig. 21:** Summary of CTE of the top coat, diffusion layer and substrates of relevance in sub-project 1. Reference: Y.S. Touloukian, R.K. Kirby, R.E. Taylor, P.D. Desai, *Thermal expansion of metallic elements and alloy*, (New York: Plenum Publishing Corporation, 1970)

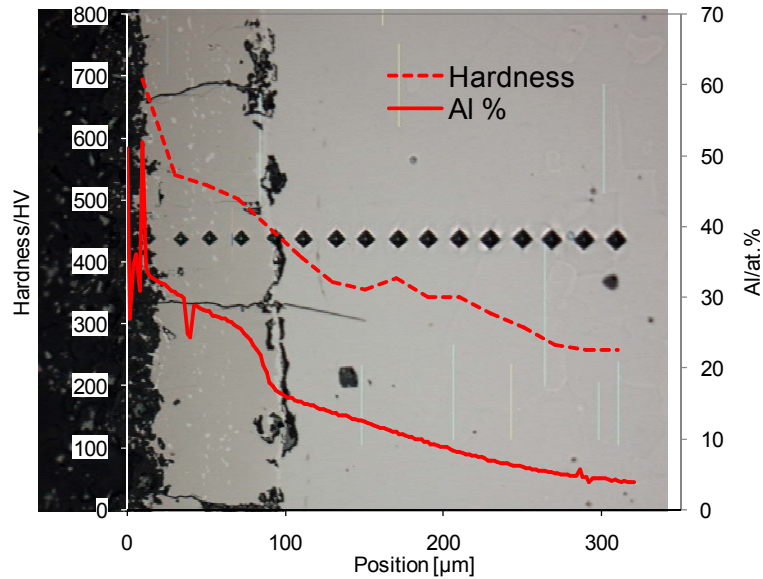
#### Micro/nano- hardness measurements

The mechanical properties of the diffusion layer have been studied by nano- and micro-hardness measurements on nickel and iron base alloys. Young's modulus has been calculated from the nano-indentation measurements. DFI has carried out the series of analyses summarized in table 4:

**Table 4:** Summary of mechanical tests carried out at DFI for evaluating the developed PARTICOAT coating designs.

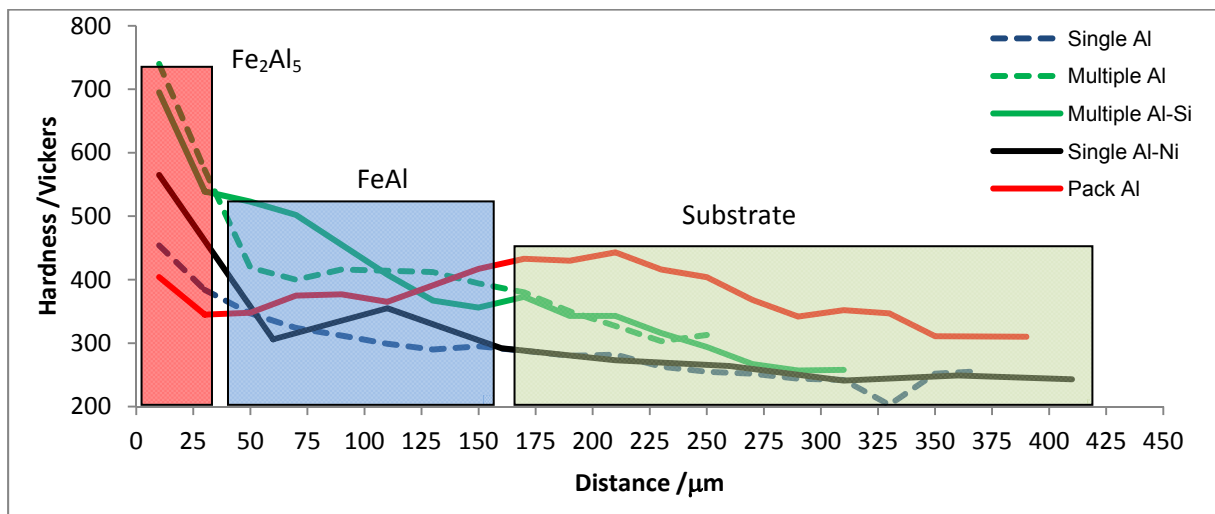
Substrate	Tested coating	Particle size/ $\mu\text{m}$	Isothermal tests
CM247 IN738 Rene 80	Al	20	800°C Air
CM247	Al	20-50	1000°C Air 1100°C Air
AISI446	Al	20 20-50	800°C Air
	Al pack	-	
	Al-Ni	20	
	Al-Si	30-50	

Micro-hardness measurements are very appropriate to determine the properties of the diffusion layer. As shown in figure 22, they not only can provide information about the hardness of the formed diffusion layer but this information could be directly correlated with the Al content of the same layer. The advantage of using the nano-indenter is that additional information as the Young's moduli of the formed phases can also be calculated.



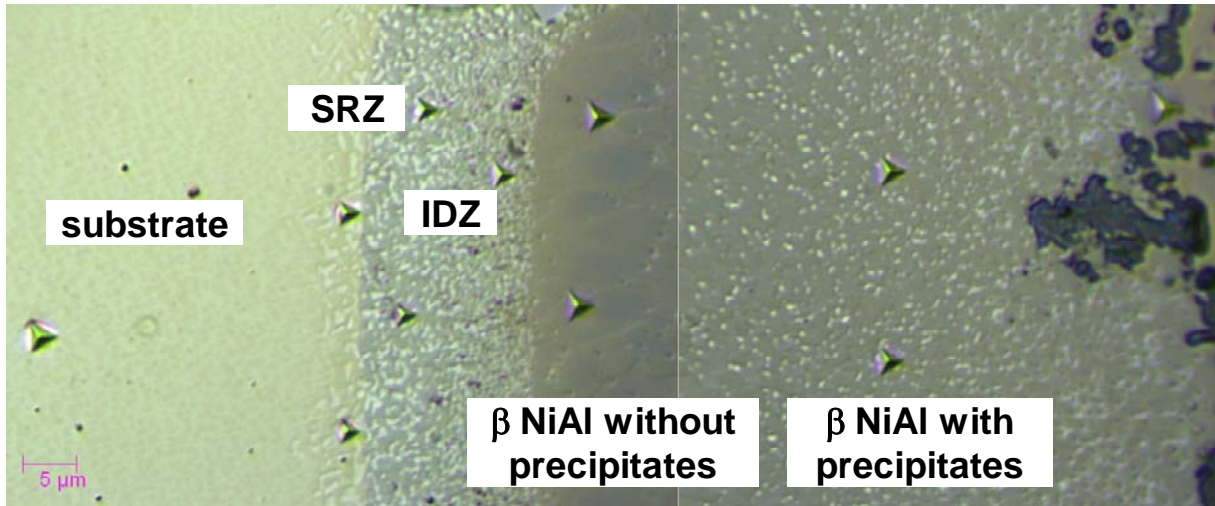
**Fig. 22:** SEM cross-section of multiple Al-Si size powder coated AISI446 exposed for 1057 hours in air at 800°C, with superposed Al profile (at.%) and hardness measurements.

Figure 23 shows the hardness measured for the different coatings developed on iron base alloy AISI446 as a function of thickness. The values are compared with those measured for the  $Fe_2Al_5$ , FeAl and AISI446 phases (phases usually found in the produced coatings).



**Fig. 23:** Hardness measurement line-scans of different Al base slurries coated AISI 446 after exposure at 800°C for 1000 hours in air, superposed to the values of different iron aluminides.

Figure 24 shows an example of the measurements and formed phases on nickel based alloys. The observed common phase structure is a diffusion layer with a matrix of  $\beta$ -NiAl, an inter-diffusion zone with a matrix of  $Ni_3Al$ , a secondary reaction zone with Cr, W, Re rich preipitates and finally the substrate.



**Fig. 24:** Electric light microscopy cross-section of Al slurry based coating deposited onto CM 247 exposed for 1057 hours in air at 1000°C and after nano-indentation measurements.

The hardness values of the phases depends on the substrate alloy composition, as observed by comparing tables 6 and 7.

**Table 5:** Composition (wt.%) of nickel base alloys tested at DECHEMA-Forschungsinstitut

	Ni	Cr	Al	Mn	Co	Si	C	Mo	W	Ta	Ti	Others
<b>IN738</b>	Bal	16	3.4	0.2	8.5	0.3	0.17	1.7	2.6	1.7	3.4	0.9Nb0.1Zr
<b>René80</b>	Bal	14	3	-	9.5	-	0.17	4	4	-	5	-
<b>CM247</b>	Bal	8.1	5.6	-	9.2		0.07	0.5	9.5	3.2	0.7	0.015B-0.02Zr-1.4Hf

In order to correlate hardness tendencies to composition, the substrate hardness seems to increase by increasing titanium and molybdenum and decreasing aluminium quantities in the substrate. The hardness of different nickel aluminides increases by increasing the chromium and decreasing the tungsten content in the substrate.

**Table 6:** Summary of hardness values obtained after exposure of different nickel base alloys at 1000°C in air.

Phase	$\alpha$ Poisson's ratio	Substrate		
		IN738	Rene80	CM247
Substrate	0.29	204	233	173
IDZ (Ni <sub>3</sub> Al)	0.31	212	255	185
NiAl without precipitates	0.31	220	219	169
NiAl with precipitates	0.31	211	210	165

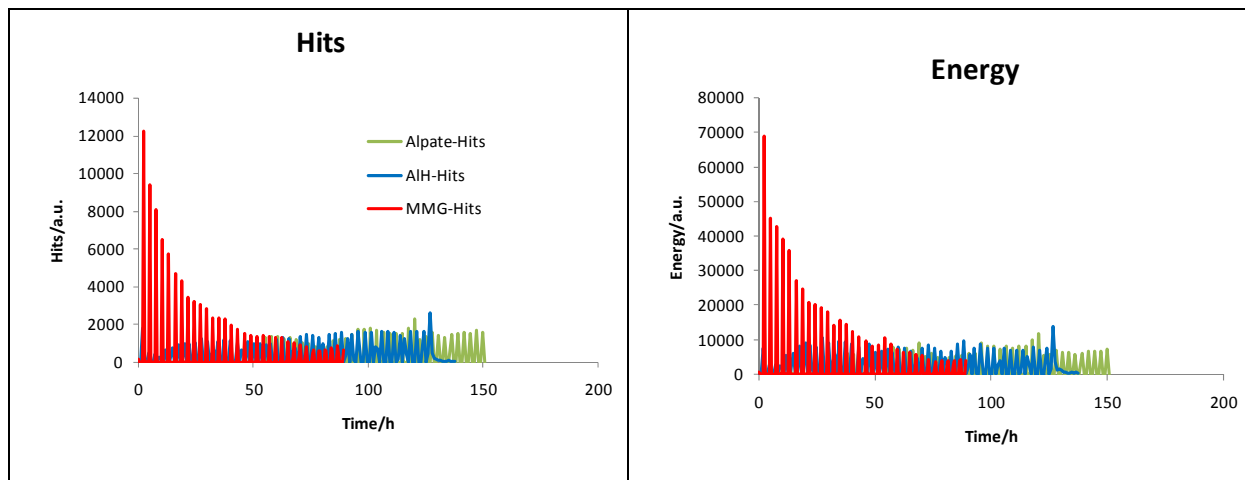
#### *Top coat mechanical properties*

The mechanical stability and adherence of the top coat were studied during thermo-cyclic exposures coupled to acoustic emission. Tests carried out are summarized in table 7.

**Table 7:** Summary of powders tested on thermo-cyclic test coupled to acoustic emission measurements in order to evaluate the adherence and crack propagation of PARTICOAT coating on nickel base alloys.

Substrate	Tested coatings				Thermo-cyclic tests
	Source	code	Particle size/ $\mu\text{m}$	spherical	
CM247 (Ni-base)	Al	0811-19	2-3	Yes	1100°C Air 1 hour heat 15 min cool
		0911-35	20	Yes	
		MMG	10-20	Yes	
		Alpate	15-50	No	
		Aluminium Hermillon	20-50	yes	

Coatings manufactured with different particles perform differently. 0811-19 and 0911-35 showed spallation since the beginning of the test (see fig. 25). MMG has shown large crack propagation. Alpate and Poudres Hermillon have shown the lowest crack propagation with similar energies. These coatings were adherent after 300 hours of exposure. Acoustic emission demonstrates that for air produced coatings the adequate source particles size ranges between 20 to 50  $\mu\text{m}$ , and at this size range, the particle form does not have a big influence.



**Fig. 25:** Acoustic emission signals during thermo-cyclic exposure on PARTICOAT coatings deposited onto nickel base alloys.

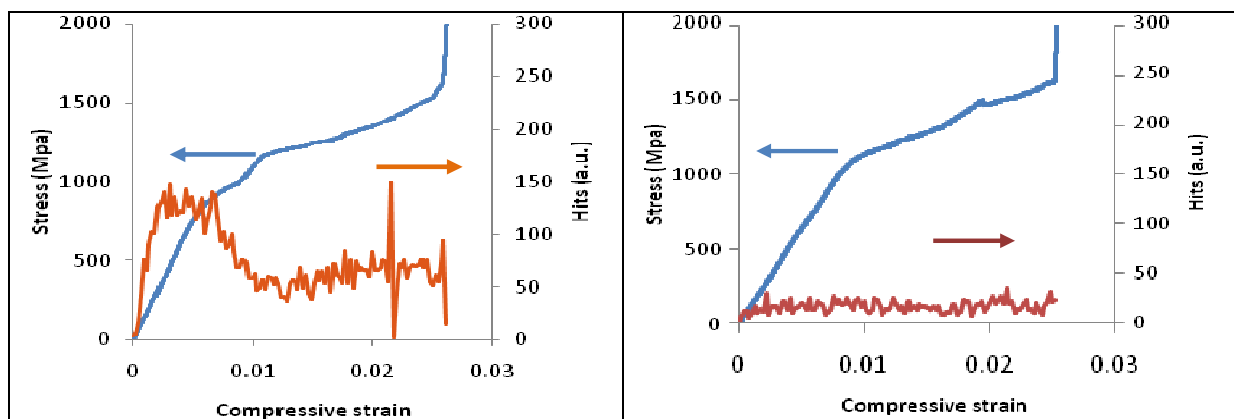
Four point bending tests coupled to acoustic emission were also carried out in order to compare the top coat and mechanical behaviour of the diffusion layer with state of the art TBC coatings. The tests carried out are summarized in table 8.

**Table 8:** Summary of powders tested on four point bending test coupled to acoustic emission measurements in order to evaluate the adherence and crack propagation of PARTICOAT coating on nickel base alloys.

Substrate	Tested coatings				Exposure before 4PB-AE test
	Source	code	Particle size/ $\mu\text{m}$	spherical	
CM247 (Ni-base)	Al	0911-35	20	Yes	1100°C Air 100h With top coat Without top coat
		Aluminium Hermillon	20-50	yes	



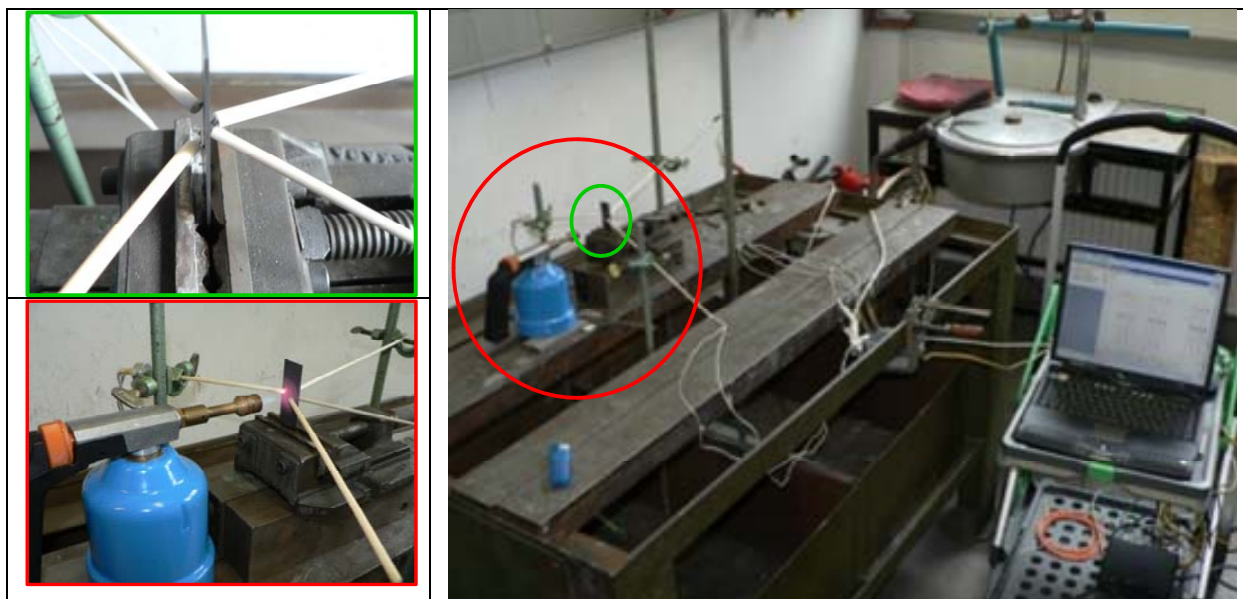
Traditionally, acoustic emission measurements coupled to four point bending measurements are used to determine the moment, in which the cracking of the top coats begins to propagate and finally breaks through. The special case of the PARTICOAT top coat, in which the top coat is an alumina foam, produces cracks continuously during the four point bending (4PB) test. Therefore, acoustic emission is also continuously measured and no clear beginning of top coat breaking or final break through can be determined (see fig.26). However, it is possible to observe the influence of the source particle size on the propagation of the cracks during the 4PB measurement. With the smaller Al source particle size, the number of cracks or hits is clearly higher than for the bigger Al particle size. This effect is controlled by the porosity of the top coat foam. Cracks propagate faster in dense materials than in porous ones. The porosity of the top coat increases by increasing the source particle size. Therefore, coating produce by smaller source particles have a higher tendency of crack propagation.



**Fig. 26:** 4PB coupled to AE of single sized ( $5\ \mu\text{m}$ ) and multiple sized ( $20\ \mu\text{m}$ ) Al powder slurry coated CM247 after 100 hours of exposure at  $1100^\circ\text{C}$  in air.

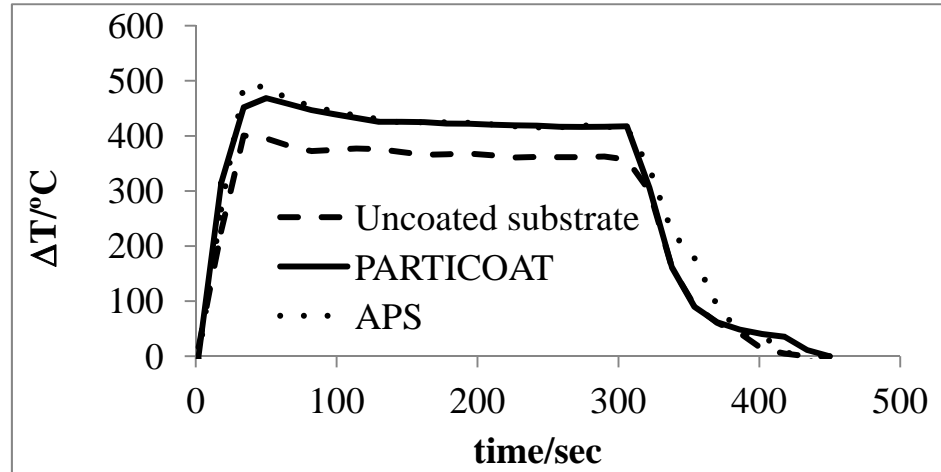
### Work package 5.3: Thermal barrier effect

DECHEMA-Forschungsinstitut tested the thermal barrier effect of the PARTICOAT coatings. The coatings were characterized by exposing one coated side to a butane flame (approx.  $1000^\circ\text{C}$ ). Temperature was measured with four thermocouples, two in the front (coated side) and two in the back (uncoated) of the samples as shown in figure 27.



**Fig. 27:** Experimental procedure to measure the thermal barrier effect of PARTICOAT coatings on metallic substrates.

The temperature difference between the front and back of an uncoated Ni base alloy (CM247) is around 380°C (see figure 28). The same alloy substrate (and thickness) coated with PARTICOAT multiple Al sized powder and atmospheric plasma spray YPSZ shows a temperature difference of 460°C. This result confirms the thermal barrier effect of the PARTICOAT based alumina foam top coat and equals the quantitative effect with the traditional dense APS produced YPSZ.



**Fig. 28:** Temperature difference between the front and the back of a CM247 Ni-based alloy, uncoated, with PARTICOAT and APS produced coatings exposed to a 1000°C flame.

The exact quantification of the heat conductivity was not carried out at the DECHEMA-Forschungsinstitut. However, this simple test demonstrates the thermal barrier effect of the PARTICOAT developed top coat.

### Work package 5.5: Modelling

The modelling tool used at DECHEMA-Forschungsinstitut has been developed previously for APS top coatings. The use of this tool could not be directly extrapolated to the PARTICOAT developed coatings, because of the differences observed in the behaviour between both top coats. Therefore, several meetings were carried out with ULR and RISK-T in order to select the appropriate model and characterization method for describing the life-time of PARTICOAT coated Ni-base alloys. The main conclusions and tasks according to the discussions were:

- There are a mechanical and a chemical parameter which determines the life-time of the PARTICOAT coatings. The mechanical is related to the thermally grown oxide thickness, which provokes the spallation of the top coat. The chemical is the aluminium reservoir in the diffusion layer, which below a certain level provokes fast growing oxides on the thermally grown oxide and consequently spallation of the top coat.
- ULR and DFI have defined a characterization and quantification method in order to analyze Al depletion in the diffusion layer.
- RISK-T use existing mathematical models in order to fit experimental results
- DFI has provided all the necessary information about the weight gain at different temperatures and post-mortem analysis of PARTICOAT coated nickel base alloys to RISK-T in order to describe the coatings life time.

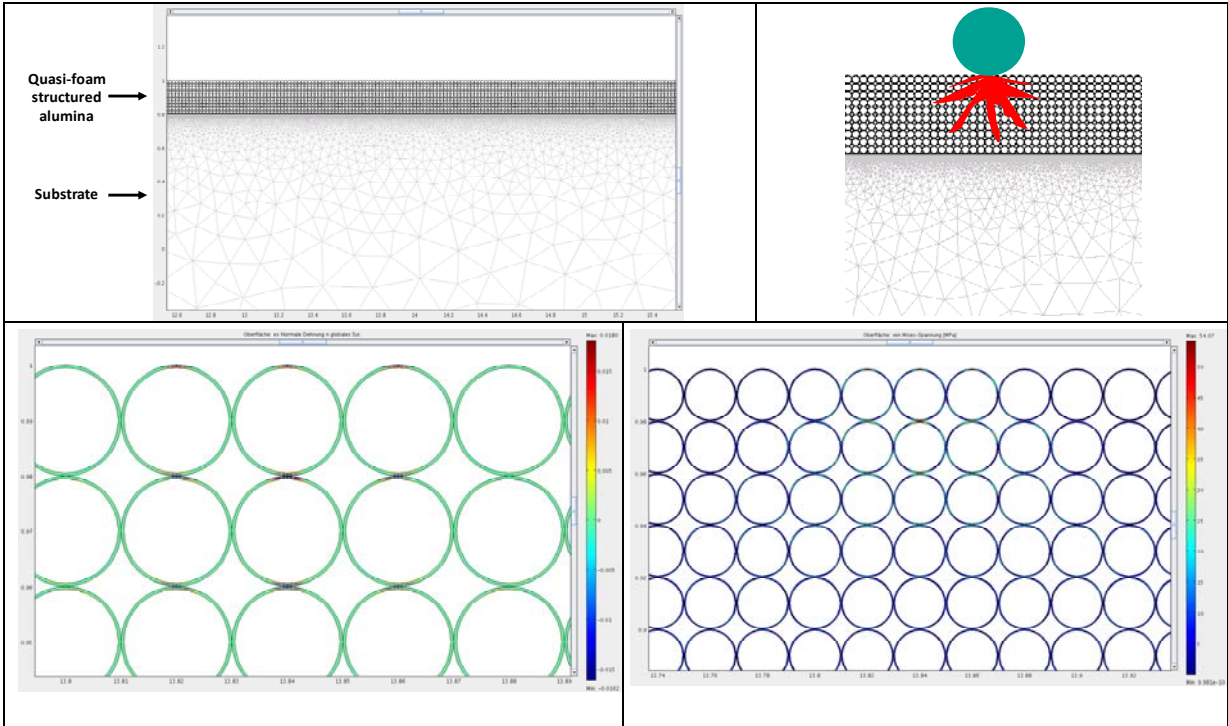
The methodology followed by DFI in order to obtain an adequate model for the life-time estimation of the PARTICOAT coatings on Ni base alloys is summarized in table 9.

**Table 9:** Summary of tests carried out at DFI for modeling PARTICOAT coating life-time.

Characterization method	Modelled parameter	Searched information	Modelling tool
ESMA	Bond coat depletion of Aluminium	Element profile	Kinetics 1.0 Bond Coat AI Simulation 1.0
Image analysis		Hardness profile	
Micro-nano indenter			
Cyclic test coupled to AE	Thermal ageing	Top coat crack propagation	Thermal Barrier Coating Lifetime Analysis 1.0
	Top coat crack propagation	Simulation	COMSOL 4.2

DFI simulated the degradation mechanisms of the PARTICOAT top coats and their crack propagation (see fig. 29). The used program was COMSOL with the version 4.2. The simulated coating consisted on a top coat based of spherical hollow particles in direct contact with the metallic substrate. Top coat thickness of 200  $\mu\text{m}$  and spherical particles with 20  $\mu\text{m}$  diameter. As observed in the next figure the particles are in direct narrow contact between them (sintered). Their oxide shell thickness (after SEM cross-section analyses was 200nm).

0.01N force application was simulated on top of such coating, simulating the case of 4 PB experiments. The simulation results showed that the main stress and strain were localized on top of oxide shells. The depth of the applied stress affected 80  $\mu\text{m}$  of the coating and the width affected was of 60  $\mu\text{m}$  coating. These observations allowed the conclusion that the substrate is unaffected by the applied pressure.



**Fig. 29:** Top coat crack propagation simulation results. System design and meshing (top left), applied force (top right), strain in X direction (bottom, left) and stress distribution in particles according to Von Mises criterion (bottom, right).

## Sub project 2:

### **Work package 7:** Particle production for fire protection

DECHEMA-Forschungsinstitut selected particle materials for fire protection in respect to both flammability retardant as well as heat protection properties. DFI contributed to the coating design for fire protection and carried out oxidation tests in thermogravimetric furnaces with different aluminium particles to obtain alumina hollow spheres.

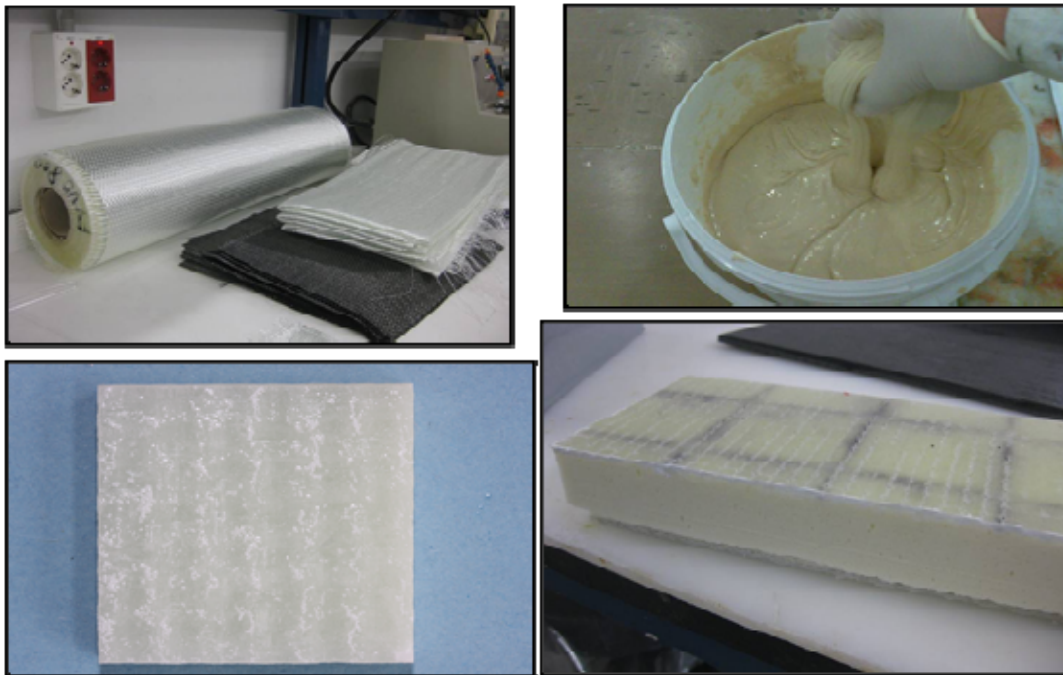
#### *Particle selection*

Oxidized aluminium particles produced during the work package 3 were used a hollow alumina as first approach. DFI has carried out oxidation tests in thermogravimetric furnaces with different aluminium particles to obtain alumina hollow spheres. The experimental conditions allowed the formation of hollow spheres from different sized aluminium particles. The particles were strongly sintered together and consequently useless for the targeted application. Therefore, alternative suppliers of commercial hollow ceramic sphere particles were selected. Anyway, the studies carried out were very helpful in order to elucidate the mechanisms involved in the PARTICOAT slurry route coating on iron and nickel base alloys.

DFI has obtained some ceramic hollow spheres by an alternative supplier. The company C. H. Erbslöh KG in Krefeld (Germany) produces alumina-silica hollow particles (36-40%  $\text{Al}_2\text{O}_3$ ; 55-60%  $\text{SiO}_2$ ; 04-05 %  $\text{Fe}_2\text{O}_3$ ; 1.4-1.6  $\text{TiO}_2$ ) in different sizes. The purchased sizes have about 45  $\mu\text{m}$  in diameter.

#### *Coating designs*

The targeted substrate material is going to be a composite sandwich shown in figure 30. The sandwich will be based on a polyurethane matrix assembled between two glass fiber plates. The glass fiber plate is formed by multilayered glass fiber laminate, assembled with an epoxy resin. The reason for adding the epoxy resin to the glass fiber is to improve the link of the multi layered structure and to give rigidity to the assembled laminate.



**Fig. 30:** Pictures of the materials forming the composite substrate for the sub-project 2 PARTICOAT application. Glass or carbon fibers (top left). Epoxy resin for assembling the glass or carbon fibers (top right). An assembled glass fiber laminate (bottom left). A composite sample with the polyurethane matrix-glass fiber sandwich structure (bottom right).

The coating designs are summarized in figure 31. The first targeted design is to coat the composite material directly by hollow ceramic spheres. The aim of this structure is to obtain a coating which avoids or retards the ignition of the composite substrate by a thermal barrier effect, produced by the spherical ceramic particle structure. Probably with such a coating structure the targeted objective to retard ignition could not be totally fulfilled; therefore, other two layer coating models were also planned. A fire retardant layer deposited on top of the hollow spheres one could serve as an intermediate coating to improve the ignition delay of the coatings and decrease the heat transfer.

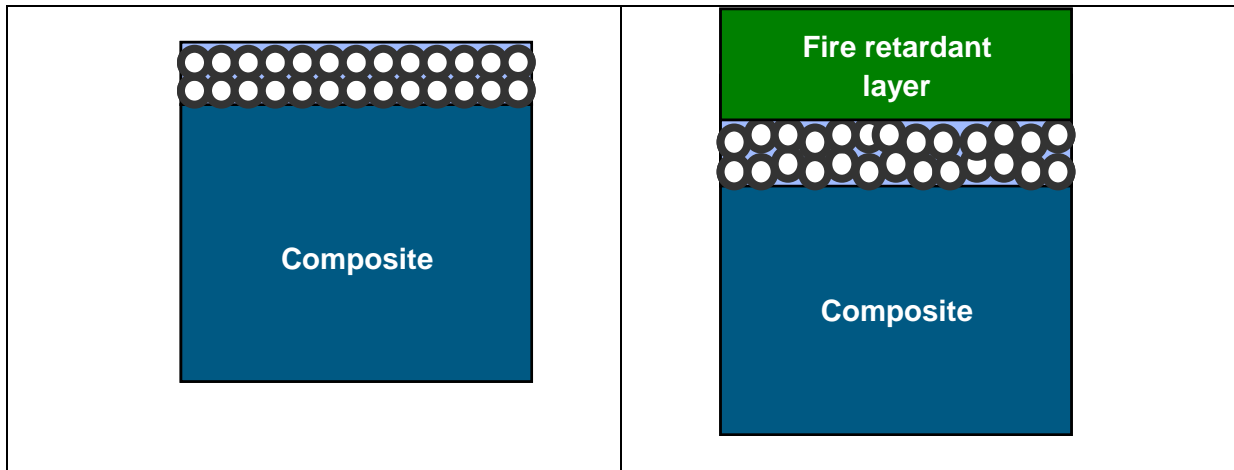


Fig. 31: Coating designs for the sub-project 2

### Work package 8: Deposition on composites

The work carried out at DECHEMA-Forschungsinstitut is summarized as follows:

- Slurry composition investigation
- Short qualitative fire protective tests of the newly developed coatings under butane flame (1000-1200°C)
- Optimization of the coating design based on the initial WP7 designs
- Transfer of the improved design and compositions to Fraunhofer ICT and to Acciona

#### *Slurry composition*

DFI has investigated different methods to produce the coatings described in WP7. Simple methods as stopping, spraying or painting were selected due to the experience acquired during work package 4.

New slurries have to be developed to reach the industrial requirements of these coatings. The binder should not decompose at low temperatures, nevertheless according to the results presented in work package 4, all organic binders decompose at temperatures above 400°C. Because it must still be present at a target temperature of 1200°C, a new selection of binders based on **inorganic materials** has been tested to develop adequate slurries. The coatings are deposited on glass fiber-epoxy laminates (40x40x10 mm<sup>3</sup>). Therefore, the selected binder must also have a **low temperature curing** property, because at temperatures above 100°C the glass-fiber-epoxy laminates are damaged and their mechanical properties decrease.

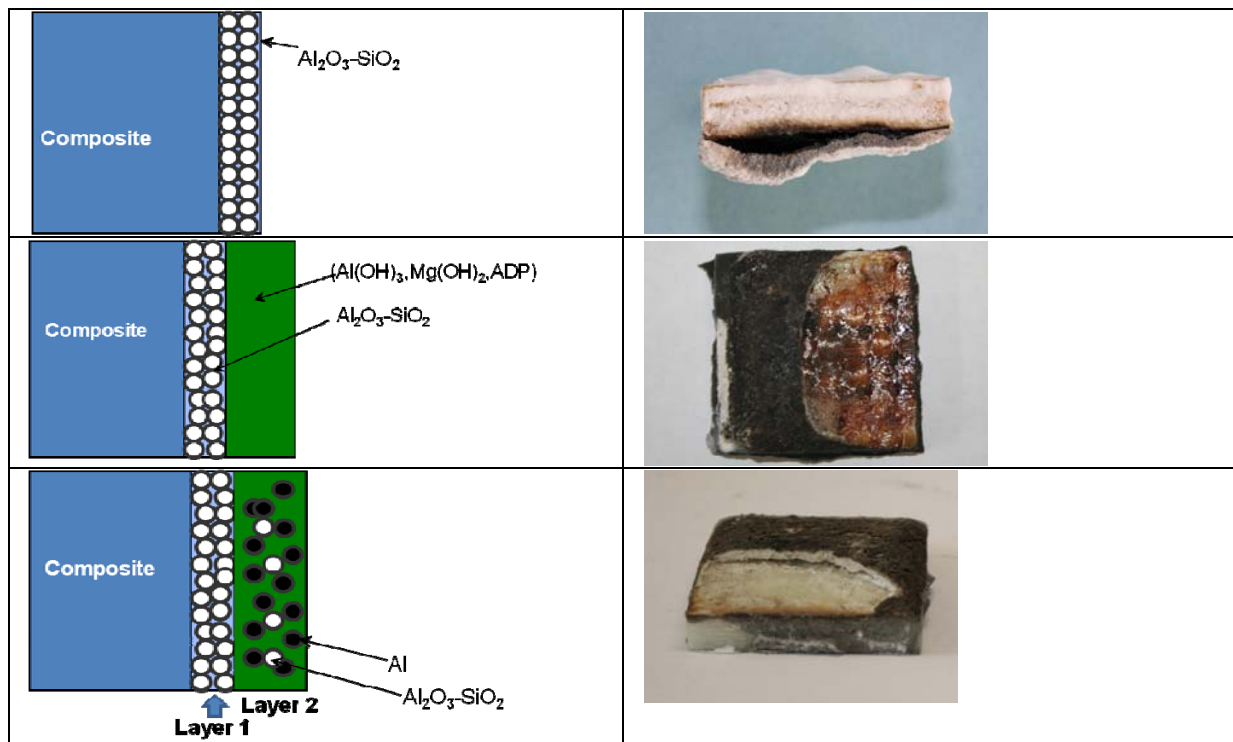
Two industrial inorganic binders exhibiting the previously explained properties were tested. The first binder is the alumina based Ceramabind 644A. The tested slurries were based on

different quantities of this binder and alumina base particles. The slurry did not adhere to the glass fiber-epoxy surface. The second binder tested, is the phosphoric acid based Ceramabind 540. In this case, the binder maintained good adherence after thermal treatment for curing at 100°C for two hours. Two different kinds of powders were tested to obtain the slurries based on Ceramabind 540. The first powder is that consisting of hollow sphere shaped alumina-silica, previously mentioned (see work package 7 for more details). The second one is an  $\alpha$ -alumina flake shaped powder. The objective of using these two powders was to demonstrate the importance to use hollow ceramic spheres for the application of fire protection as a thermal barrier because of its gas isolation effect.

The use of the alumina-silica hollow spheres still seems to be encouraging due to the potential of such hollow spheres as heat transfer retardants through the substrate. Therefore, the coatings designed by DFI consisted of a first layer of alumina-silica hollow sphere particles based coating directly deposited onto the composite substrate and a second layer of different flame retardant materials. This combined coating could thus provide a double effect of ignition and heat transfer retardant. In order to avoid the problem of the inhomogeneous heat transfer through the flame retardant coating DFI has produced a final design which combines metallic particles with the flame retardant material on the top layer

#### *Optimization of the slurry composition*

DFI tested and optimized the coatings depending on the results obtained from fire exposure experiments. The first coatings designed by DFI consisted of an alumina-silica hollow sphere particles based coating directly deposited onto the composite substrate (Fig. 32). The low temperature needed for curing the selected binder (around 200°C) and the possibility of producing thick coatings (up to 1 cm) showed very interesting manufacturing properties for this coating. However, the fire tests carried out at around 1000°C (butane flame) demonstrated the low time efficiency of the coating as fire protection. As observed in Fig. 32 the coating lost adherence due to the large amount of smoke produced by the burning of the substrate composite. The use of the alumina-silica hollow spheres still seemed to be interesting due to the potential of such hollow spheres as heat transfer retardants through the substrate. Therefore, the next coatings designed by DFI consisted of a first layer of the same alumina-silica hollow sphere particles based coating directly deposited onto the composite substrate and a second layer of different flame retardant materials (see figure 32). This combined coating could thus provide a double effect of ignition and heat transfer retardant. The tested flame retardant materials were  $\text{Al}(\text{OH})_3$ ,  $\text{Mg}(\text{OH})_2$  or aluminium diphosphate. However, the fire tests carried out at around 1000°C (butane flame) demonstrated the inefficiency of the flame retardant materials due to an inhomogeneous heat transfer through them. The first layer reacted dissimilarly and the substrate composite burned out as observed in Fig. 32. In order to avoid the problem of the inhomogeneous heat transfer of heat through the flame retardant coating DFI has produced a final composition which combines metallic particles with the flame retardant material on the top layer (Fig. 32). The fire tests demonstrated the excellent properties of the flame retardant materials. As observed in figure 32 the substrate composite did not burn after 10 minutes of exposure and a low amount of smoke was produced during the burning test. The top coat was removed after the use of a hammer, which gives a qualitative idea of the adherence of the coating.



**Fig. 32:** Fire protection design based on a multiple layer coating being the first of alumina silica hollow spheres and the second a homogeneous reaction flame retardant materials based layer (left) and photography of the coating after fire exposure at 1000°C for 7 minutes (right).

Samples with different dimensions and compositions (see table 10) based on this coating design have been sent to Fraunhofer ICT to obtain quantitative measurements of fire protection and to Acciona to carry out ISO standardized tests in order to confirm their applicability for fire protection and adhesion criteria in airplanes, hospitals or buildings.

**Table 10:** Summary of coating parameters for obtaining reproducibly of the two coating designs developed at DFI.

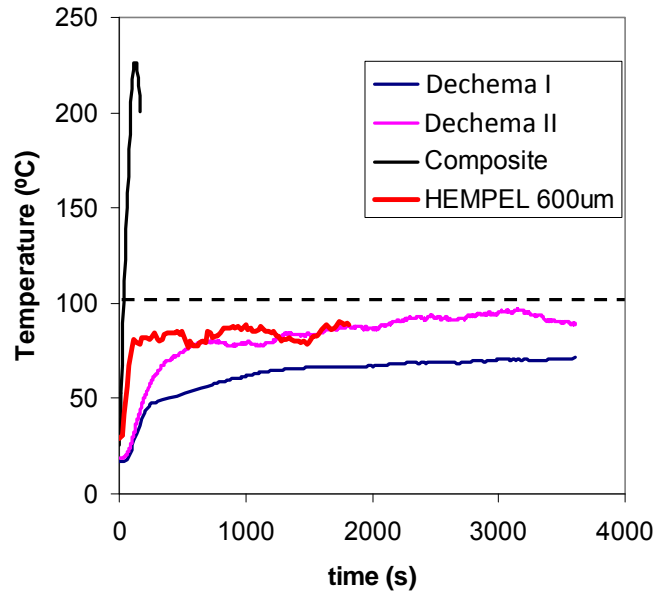
		Alumina-silica hollow sphere	Ceramabind 542	Epoxy	Amonium phosphate	Aluminium spheres
I	First layer	50	50	-	-	-
	Second layer	10	-	40	40	10
II	First layer	50	50	-	-	-
	Second layer	-	-	40	50	10

Acciona has measured by standard methods the fire resistance of the two compositions coatings given at table 10. The results of the fire tests were compared with state of the art and uncoated samples (see figure 33) showing very promising results. The Dechema II composition behaves similar to the state of the art coating and the Dechema I coatings improves the state of the art coating by 20°C.

Conclusions for the work carried out during the SP2 at DFI are:

- The coatings produced are easy to manufacture giving good surface finishing, easy to manipulate by the employees and non-harmful due to the non volatile organic nature of their composition and absence of halogens.
- The chemical and mechanical compatibility between the composite used as substrate and the developed coating is excellent.
- After qualitative burning exposures in butane flame at DFI, no dripping or substrate composite degradation was observed.

- The previously cited properties and the low toxicity of the smoke produced describe the high potential of the developed coatings as protection for buildings.
- High potential of the developed coatings for protection of buildings was demonstrated after the normalized fire resistance tests carried out in Acciona.



**Fig. 33:** Temperature difference between the front and the back of uncoated (Composite), state of the art coated (HEMPEL) and Dechema design coated composites measured in Acciona during fire exposure at 1000°C (normalized method).

**Sub project 3:**

**Work package 10:** Coating design and particle processing for electrical insulation

DECHEMA-Forschungsinstitut developed coating designs and identified possible particle suppliers to produce a prototype series of coatings.

*Introduction*

The key application of interest for the new coatings is the water cooled tube-pipes used for the power supply in Ni-production. An electrical insulation problem that leads to severe degradation of the Cu tube-pipes used for the power supply in Ni-production was described by Larco. A very pure Cu alloy (99,95% Cu, exact properties and composition are given in table 11) is used in atmospheric conditions.

**Table 11:** Composition and properties of the copper alloy, used by LARCO

Chemical composition:	Density	Melting Point	Thermal Expansion Coefficient:	Heat capacity:	Electrical Conductivity:
Cu (%) ≥ 99.95 P (%) = 0.002 – 0.007 Bi (%) = 0.0005 Pb(%) = 0.005 Total impurities = 0.03	8.94 g/cm <sup>3</sup> at 20°C	1083°C	From 20 to 100°C = 16.9 *10 <sup>-6</sup> K <sup>-1</sup> From 100 to 200°C = 17.3 *10 <sup>-6</sup> K <sup>-1</sup> From 200 to 300°C = 17.6 *10 <sup>-6</sup> K <sup>-1</sup>	From 20 to 100°C = 0.385J/(g•K) From 100 to 200°C = 0.393 J/(g•K) From 200 to 300°C = 0.403 J/(g•K)	From 20 to 100°C = 57-55 MS/m From 100 to 200°C = 43.6 MS/m From 200 to 300°C = 33.7 MS/m



Nevertheless, the extreme harsh electrical conditions, to which these tubes are exposed, can cause spark ignitions. The operating voltages are in the range between 380-420 V and the current varies from 6.000 to 8.000 A. In these conditions the Cu-tubes have to resist flames, sparks dust and high temperatures, as illustrated in Figure 34.



**Fig. 34:** Spark Ignitions on the power supply of electric arc furnaces in the Nickel production process (LARCO)

Especially spark ignitions cause severe problems in the production of Nickel. In 2008, Larco had to stop its production 24 times due to spark ignitions; each time for about 8-36 hrs. Usually 10 tons of Nickel are produced per day, which means an annual loss of 4.000.000 - 5.000.000 \$ caused by these incidents.

The coatings have to be applied on cylindrical copper tubes having an external diameter of 50 mm and an internal diameter of 30 mm. They operate under extremely high current and voltage in an environment containing dust and flames at very high temperatures. At the moment an insulation transformer varnish is applied to the tubes by brushing. It offers electrical insulation, but flames and particle erosion often destroy it. Therefore the new coatings must provide heat resistance, electrical insulation and abrasion resistance in combination with a cost efficient application technique.

#### *Coating designs*

For the first model, illustrated in fig. 35, the aluminium powder obtained in work package 3 will be directly applied onto the substrate, specified by the industrial partners for sub-project 3 (copper rich alloy). After a heat treatment, the deposited aluminium spheres will form an alumina hollow spheres top coat and a diffusion zone, rich in aluminium. According to the industrial specifications the alumina hollow sphere thickness should not exceed 100  $\mu\text{m}$ .

In the second model, a mixture of aluminium and silicon is coated on top of the substrate. The aim of this mixture is to obtain a coating with glassy structure that could serve as sealant after the heat treatment. Therefore, slurries based in silicon binders or silicon powder has to be mixed with the aluminium powder obtained in work package 3.

The third model, see fig. 35, is based on the application of previously formed ceramic hollow spheres on top of the copper substrate. These hollow spheres will be obtained from work package 3. The investigated powders were zirconia based hollow spheres. After a heat treatment, the deposited ceramic hollow spheres sinter. The deposition method and the slurries were directly obtained from the experimental results of work package 4 as well as from Pyrogenesis know how.

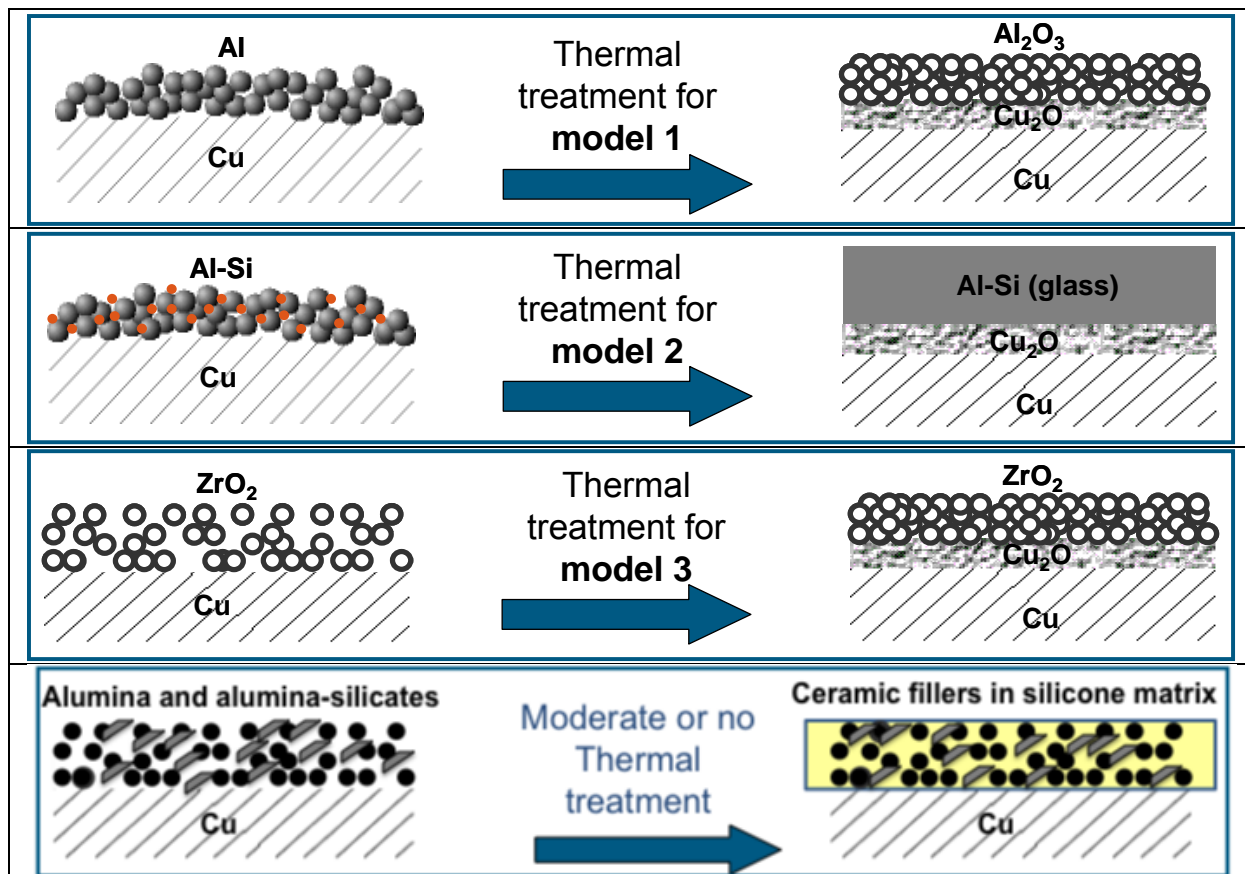


Fig. 35: Electrical insulation coatings design developed at DECHEMA-Forschungsinstitut for sub-project 3.

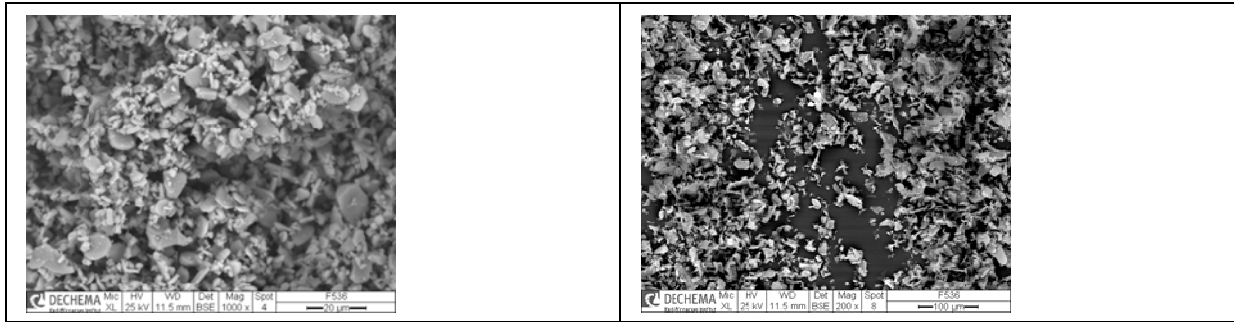
According to the industrial application at LARCO, it is highly important to produce a coating that does not need of an initial heat treatment. The previously described three models unfortunately need a heat treatment to produce the hollow ceramic structure or to sinter them. Therefore, a new model has also been developed based on the outputs and knowledge obtained from the studies of the previous models. The model relays the deposition of a bimodal coating, consisting of alumina and mica. The coating design developed by DFI is shown in figure 35. Two different set of coatings were sent to PyroGenesis and LARCO in order to be electrically and mechanically characterized, mainly differentiated by the need or not of a heat treatment.

#### Work package 11: Deposition procedure for electrical insulation

DECHEMA-Forschungsinstitut formulated coating compositions to deposit adherent layers with the capability of electrical insulation with no need of heat-up. Deposition methods, such as brushing or spraying were investigated, however, due to the differences in slurry composition the knowledge from WP4 could not be directly applied. DFI investigated the coating manufacturing at laboratory scale and characterise the coating microstructure. Samples coated with those compositions were sent to LARCO and Pirogenesis in order to perform mechanical and electrical resistance tests. The successful formulations were modified in order to be applied and tested in field.

#### Slurry composition

The fillers were selected according to their high electrical insulation properties and mechanical properties. They consist of alumina, mica or a combination of both. In any case the spherical hollow particles were not further investigated due to their bad electrical insulation. The selected alumina and mica are shown in figure 36.



**Fig. 36:** Powder sources used at DFI. Al<sub>2</sub>O<sub>3</sub> (left) and Mica (right)

The deposition parameters of the DFI designed electrical isolation coatings are summarized in table 12.

**Table 12:** Summary of coating parameters examined to obtain the coating designs developed at DFI.

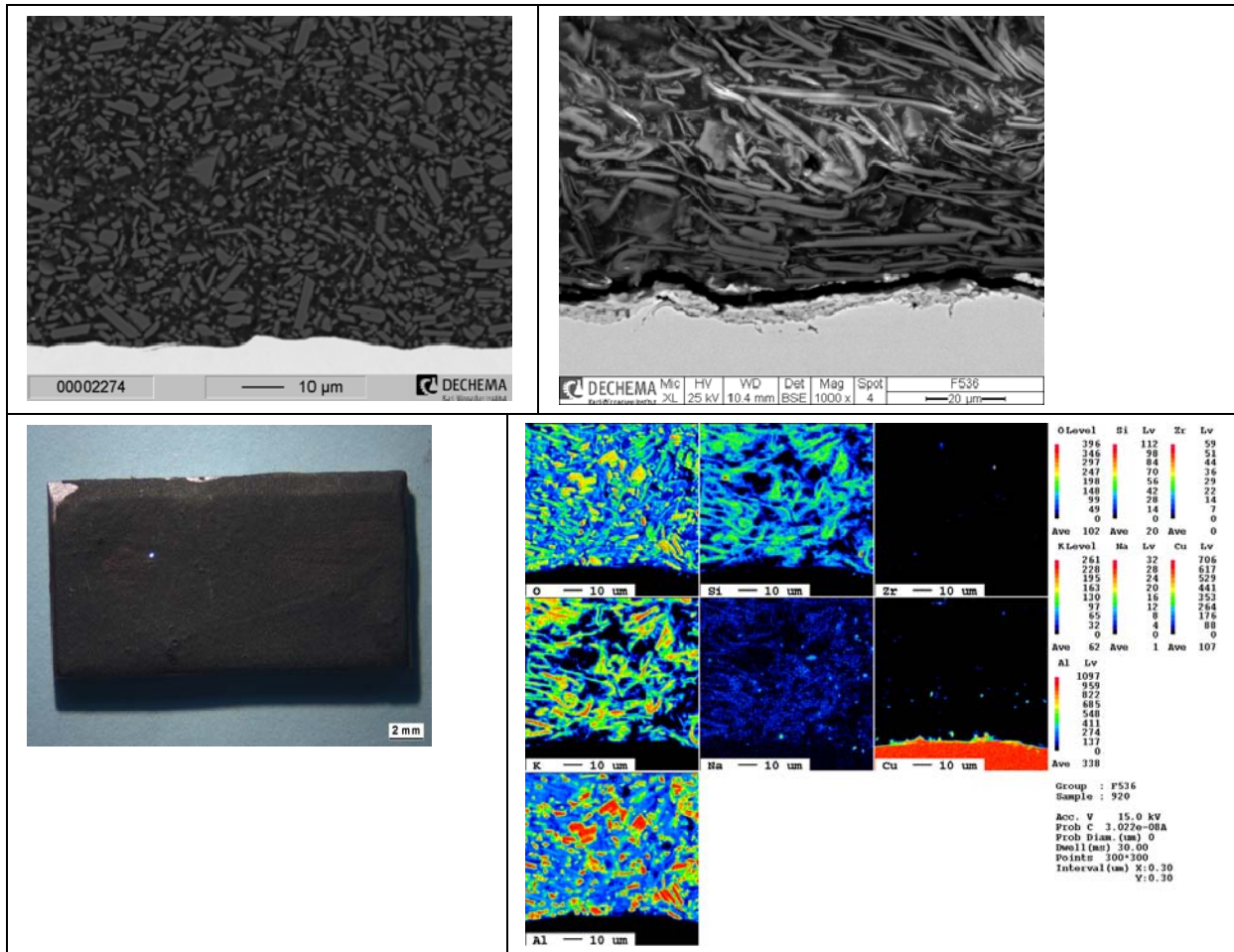
Substrate	Substrate pre-treatment	Powder	Powder size	Binder	Coating method	Heat treatment
Cu	Degreased with ethanol	Al <sub>2</sub> O <sub>3</sub> Mica (laminar alumina silicate)	20 μm	Silikophen P50/X	Paint	200°C air
				Silikopon EF		none

As observed in figure 37 the coatings are easy to manufacture by air brushing or painting, they show excellent adherence with the copper substrate and good finishing, allowing easy manipulability and applicability of full coatings which could eventually also be used to repair locally damaged copper tubes by the employees in the plant. It forms a glassy structure when exposed to high temperatures. This property could be very beneficial for the industrial application due to the spark ignition episodes usually produced at LARCO.



**Fig. 37:** Copper cylinder coated by electrical insulation layer sintered at 200°C

The alumina based coatings have shown good adherence while the mica based coatings showed adherence problems due to the flake oriented shape. Mica flakes align parallel to the surface of the copper substrate which has a negative effect on the adherence (see figure 38). However, due to the important electrical resistance properties that characterizes the mica and its beneficial effect on viscosity and manufacturing, also various combinations of both has been tested. At an optimized ratio the detrimental orientation of the mica flakes could be avoided due to the Al<sub>2</sub>O<sub>3</sub> particles as shown in the model design of figure 38. A elemental mapping of the combined Al<sub>2</sub>O<sub>3</sub>-mica based coating is shown in figure 38.



**Fig. 38:** SEM cross-section of multiple Al<sub>2</sub>O<sub>3</sub> (top, left) and mica (top, right) slurry based coated copper by using a room temperature curing binder. Surface macro-picture after heating to 300°C to test the thermal stability (bottom, left) and EPMA cross-section (bottom, right) of multiple Al<sub>2</sub>O<sub>3</sub>-mica slurry based coated copper by using a room temperature curing binder.

Mechanical tests (carried out by PyroGenesis) and the electrical tests (carried out by LARCO) shown that all the coatings developed by DFI match the eligibility criteria. However, the “in situ” application of the coatings is specified by LARCO in order to produce the coatings directly in the plant and without the need heat treatments. This heat treatment is overcome by the use of a room temperature cross-linking silicone hardener.

The first electrical resistance measurements of the coatings carried out at LARCO obtained around 200 GΩ of electrical resistance, demonstrating the excellent insulation properties of the developed coatings. The adherence was between 17-19 MPa for the coatings without heat treatment and 29-34 MPa for the coatings with heat treatment. These adherence values are very similar to the APS coated PYSZ used in land-based gas turbines, demonstrating the excellent adherence of the coatings. The erosion resistance and the resistance against fire were also excellent (see PyroGenesis report for more information).

DFI helped in the up-scaling process from laboratory to industrial applications in order to be tested at the LARCO consortium industrial partner and provided LARCO with the necessary information and assistance in order to apply the coating method industrially.

## Articles and conferences:

The results of these experiments were presented at international conferences and workshops and in article form.

### Conference talks:

Title	Authors	Date	Place
Particoat: New Multipurpose coating systems based on novel particle technology for extreme environments at high temperatures	X. Montero M. Schütze	30. September - 2. October 2009	European Federation of Corrosion Workshop EFC-Event No. 321 DECHEMA-Haus, Frankfurt am Main.
A single step process to form in-situ an alumina foam/aluminide TBC system for alloys in extreme environments at high temperatures	X. Montero M. Galetz M. Schütze	2.-6. May 2011	ICMCTF 2011 San Diego, USA
Initial Aluminizing Steps of Pure Nickel from Al Micro-Particles	G. Bonnet M. Mollard B. Rannou J. Balmain F. Pedraza X. Montero M. Galetz M. Schütze	3.-8. July 2011	Diffusion in Materials - DIMAT 2011 Dijon, France
Influence of the particles and substrate composition on the performance of new protective coating system based on micro-scale aluminium particle technology at extreme environments at high temperatures	X. Montero M. Galetz M. Schütze	5.-7. October 2011	FeAl2011, Lanzarote, Spain
Multipurpose TBC System Based in Alumina Foam Top Coat and Aluminium Rich Diffusion Layer Produced by Micro-Scaled Aluminium Slurries	F. Pedraza M. Schütze V. Kolarik	20-25 May 2012	8 <sup>th</sup> International Symposium on High Temperature Corrosion and Protection of Materials, Les Embiez, France
Innovative aluminide slurry coatings produced in air for nickel-based alloys	M. Galetz X. Montero M. Schütze	9.-13. September 2012	EUROCORR 2012, Istanbul,
Slurry particles tailoring to improve the performance of PARTICOAT coatings on iron base alloys at extreme environment at high temperature	X. Montero M. Galetz M. Schütze	15-17 October 2012	European Workshop: New Approaches to High Temperature Coatings Costa Teguse, Lanzarote, Spain

## Posters:

Title	Authors	Date	Place
PARTICOAT: New multipurpose coating systems based on novel particle technology for extreme environments at high temperatures	X. Montero M. Schütze	September 30 until October 2, 2009	Solutions for High Temperature Corrosion Protection in Energy Conversion Systems DECHEMA-Haus, Frankfurt am Main.
New multipurpose coating system based on novel particle technology for extreme environments at high temperatures	X. Montero M. Galetz M. Schütze	December 2010	Dechema Jahreskolloquium DECHEMA-Haus, Frankfurt am Main.
New protective coating system based on micro-scale aluminium particle technology for extreme environments at high temperatures	X. Montero M. Galetz M. Schütze	11.-13. April 2011	8th International Conference on the Microscopy of Oxidation, Liverpool/UK
New Protective Coating System Based on Micro-scale Aluminium Particle Technology for Extreme Environments at High Temperatures	X. Montero M. Galetz M. Schütze	December 2011	Dechema Jahreskolloquium DECHEMA-Haus, Frankfurt am Main.
Synthesis Of TBC System With Platinum-Modified Aluminide Bond-Coat From Water Based Slurry Onto Nickel-Based Superalloys	M. Mollard X. Montero B. Bouchaud M. Galetz J. Balmain G. Bonnet M. Schütze F. Pedraza	20-25 May 2012	8 <sup>th</sup> International Symposium on High Temperature Corrosion and Protection of Materials, Les Embiez, France
Sulphidation behaviour of non harmful water based Al and Al-Si slurry coated CM247 superalloy	X. Montero M. Galetz M. Schütze	19-21 September 2012	EFC Workshop: Beyond Single Oxidants DECHEMA-Haus, Frankfurt am Main.
Sulphidation behaviour of a non harmful water based Al and Al-Si slurry coating on CM247 superalloy	X. Montero M. Galetz M. Schütze	December 2012	Dechema Stiftungstag DECHEMA-Haus, Frankfurt am Main.
Slurry particles tailoring to improve the performance of PARTICOAT coatings on iron-base alloys at extreme environment at high temperature	X. Montero M.C. Galetz M. Schütze W. Stamm	15-17 October 2012	European Workshop: New Approaches to High Temperature Coatings Costa Teguse, Lanzarote, Spain

## Articles:

Title	Authors	Date	Place
A single step process to form in-situ an alumina foam/aluminide TBC system for alloys in extreme environments at high temperatures	X. Montero M. Galetz M. Schütze	December 25, 2011	Surface and Coatings Technology vol. 206 issue 7. p. 1586-1594
Initial Aluminizing Steps of Pure Nickel from Al Micro-Particles	G. Bonnet M. Mollard B. Rannou J. Balmain F. Pedraza X. Montero M. Galetz M. Schütze		Defect and Diffusion Forum, 323-325, (2012) 381-386
Novel processing in inert atmosphere and in air to manufacture high-activity slurry aluminide coatings modified by Pt and Pt/Ir	M. C. Galetz X. Montero H. Murakami	October 2012	Materials and Corrosion, Volume 63, Issue 10, pages 921-928
Dissolution and diffusion processes in the initial stages of slurry aluminization of nickel	M.C. Galetz X. Montero M. Mollard M. Günthner F. Pedraza M. Schütze		Submitted to Intermetallics
Sulphidation behaviour of non harmful water based Al and Al-Si slurry coated CM247 Superalloy	X. Montero M.C. Galetz M. Schütze		Submitted to Oxidation of Metals
Factors governing the particle composition selection to produce aluminides from slurry route on iron base alloys			

**Explanation of the use of the resources:**

Will be delivered in the Form C.