H2020 Innovation Action - This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N. 958457

Project acronym:	**FORGE**		
Project title:	**Development of novel coating materials for a sustainable industrial future**		
Activity:	LC-SPIRE-08-2020 Novel high-performance materials and components (RIA)		
Call:	H2020-NMBP-ST-IND-2020-singlestage		
Funding Scheme:	RIA	**Grant Agreement No:**	958457
WP1	End user requirements analysis and adaptation		

D1.4 - Review of Performance Targets/Key Performance Indicators

Due date:	3131/03/21	
Actual Submission Date:	3131/03/21	
Lead Beneficiary:	TVS	
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Dissemination Level*:	PU	
Nature:	Report	
Status of this version:		**Draft under Development**
		For Review by Coordinator
	X	**Submitted**
Version:	V1	

REVISION HISTORY

Version	Date	Main Authors/Contributors	Description of changes

* Dissemination level security:

PU – Public (e.g. on website, for publication etc.) / **PP** – Restricted to other programme participants (incl. Commission services) / **RE** – Restricted to a group specified by the consortium (incl. Commission services) / **CO** – confidential, only for members of the consortium (incl. Commission services)

CONTENTS

Summary

The FORGE project aims to synthesise novel coating materials that will extend the lifespan of material components used in energy intensive industries. This report, as a working document, details the key performance indicators (KPIs) that will be used to determine the success of the new coating materials throughout the development and optimisation stages of the project (work packages 2 to 9).

Chapter 1 will describe the methodology. The main section of this report are Chapters 2-9 and Chapter 10 which encompassesencompasses the KPI analysis of work packages 2-9 and the table of KPIs, respectively. The conclusions of the report are presented in Chapter 11.

The KPIs detailed in this report will be monitored and revised as the FORGE project advances.

Objectives Met

The deliverable contributed towards the work package objective:

- To produce and agree the Performance Targets (PTs) and Key Performance Indicators (KPIs) relevant to FORGE component performance.

1 METHODOLOGY

To demonstrate success and validation of novel materials, such as coatings for components in energy intensive industries, measurable values known Key Performance Indicators (KPIs) are used. The SMART criteria will be followed to evaluate the relevance of the KPIs:

- Specific (has the objective been clearly defined?).
- Measurable (can this be measured quantitatively or qualitatively?)
- Attainable (can the goal be reached?)
- Relevant (are the indicators appropriate to the progression of the project?)
- Time-bound (can the object be reached within a definitive time?)

A one-page word document template was prepared and then completed by all work package contributors, then discussions were held to clarify definitions and missing information. This report, for each KPI, covers the criteria (rationale and risks/mitigations), state of art (currently used materials/component type and dimensions and targets) and test and key performance indicators (testing conditions and measurement procedures, test standards/sample geometry, specimen types).

The information has been collected initially in a spreadsheet, that included information useful for internal referencing and management of the project, here not reported for confidentiality reasons. The KPIs spreadsheet was divided in three sections, the first one, in blue below, were describing more the activities related to the KPI (methodology, responsible partner, related tasks etc.). The second section, in orange below, were addressing the description of the Key Performance Indicator itself, identifying the value and the risks associated with the KPI choice. The final section in the spreadsheet, in green below, has been utilised to identify reference material or reference properties against which to benchmark the FORGE's materials. The SoA benchmarks have increasing meaning and importance moving from the initial workpackages, and arriving to the final workpackage, in which the SoA are the current solution adopted in the industry.

KPI number	KPI Name	Task(s)	Performance target	Tested by	Specimen type	Test type	Test name (standard)	Testing conditions	Standard sample geometry for testing	Other geometries possible?
				Patner		Lab/Field			L x W x T	Y/N

Quantity measured directly from test	KPI	KPI target value	KPI Units	Rationale for the selection of the KPI	Risks and limits associated with the assessment technique	Mitigation measures if risk/limit is met
				Why and how did you select this specific KPI	What risks have been identified in using this technique in the	

SOA material selected for the FORGE project	SOA KPI value	SOA cost	SOA Component type and dimensions	How often, in average, is the SOA component replaced in service?
		EUR/kg or EUR/comp		

The KPIs have been defined in each stage of the project activities but are addressing different purposes, at the early stages of development (WP2 and WP3) the KPI are mostly addressing the validation of the Machine Learning algorithms and partially addressing the identification of the most performing compositions.
The KPIs identified for the Machine Learning algorithms are addressing its robustness and reliability, in WP5 are the first KPIs related to the final result, although still in the powder stage.
The KPIs from WP5 onwardonward can be intended as threshold to be met in order to proceed with further developments or further investigation.
In WP6 are reported Key Performance Indicators of the coating performance per se, while in WP7 the test against which KPIs are evaluated, are considering the final industrial use cases.
Last KPIs are related to the industrial use, they are the final target of the project and the threshold to meet that guarantee the adoption of FROGE results by the industries involved as validators.

2 WORK PACKAGE 2

2.1 Chapters 2-9 presents an analysis of each KPI in WP2-WP9, addressing sections such as the criteria, targets based on SoA and testing standards/procedures.KPI 2.1: Hardness

Criteria

Hardness will be evaluated via Vickers Hardness (HV10), in order to compare with the values coming from the machine learning model and thus allows evaluating the machine learning model predictive capacity. The measured values should not be more than 10% from the predicted value.

An important risk is that the machine learning model is based on literature input, where the measured hardness value can depend on the actual load that was applied (where lower loads tend to lead to higher hardness values and are more prone to surface effects (oxide layers) and to scatter.

Hardness is an important first parameter to estimate the wear rate, although it is not the only parameter (and brittleness increase for the higher hardness materials might adversely affect the wear properties). Also, for the hydrogen embrittlement, hardness is an important parameter, as higher hardness materials are expected to become more vulnerable for hydrogen embrittlement.

State of Art

Not applicable yet for the first screening phase

Test and Key Performance Indicators

Hardness will be evaluated via the Vickers hardness test on all 30 induction melted samples (after casting and after homogenization thermomechanical processing), according to the ASTM E92 standard, with a load of 10 kg. Sample size is set to 12×10×5 mm, according to the internal OCAS/ARC procedure.

2.2 KPI 2.2: H_2 Charging

Criteria

Objective is to submit all 30 samples (and SoA) to a fixed charging time in a solution prepared with heavy water, measure the diffusible ((i.e. non-deeply trapped) hydrogen in all samples and rank the samples versus the SoA (stainless steel, ee.g. 316L) and each other. The underlying hypothesis is that a larger amount of diffusible hydrogen will lead to more risk of embrittlement.

The risk is that the hydrogen diffusion in the complex concentrated alloys is very slow and long charging times might be required before equilibrium through thickness is achieved. In that case, longer charging times and increased temperature are required. Some first tests on the Cantor alloy, lab processed at OCAS, can be performed.

State of Art

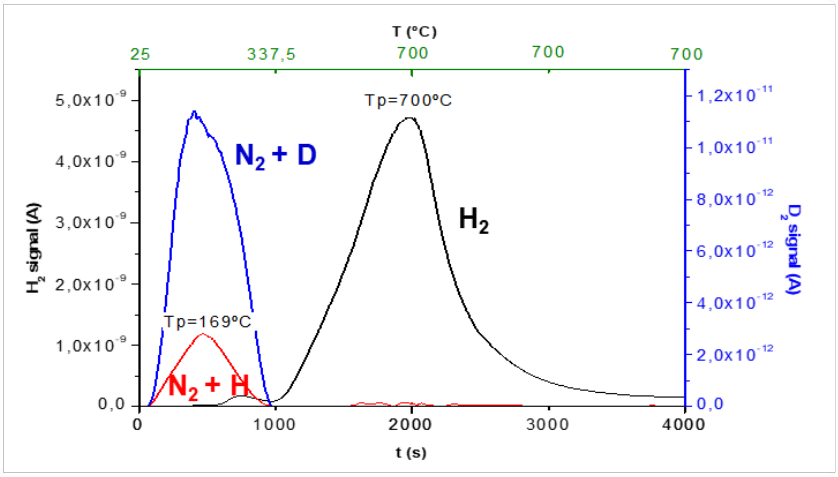
The SoA material used is stainless steel 316L, which has excellent resistance to hydrogen embrittlement (but limited strength). TheSoA KPI value (i.e. the amount of diffusible hydrogen under the applied conditions requires to be determined in the set-up).

Test and Key Performance Indicators

The test procedure consists of immersion of all samples (cast and thermo-mechanically processed to break up the heterogeneous cast structure) for a fixed time into a liquid solution with hydrogen/deuterium ('heavy water'). The use of deuterium instead of hydrogen, which reduces the significantly the noise during measurement afterwards. After charging, samples will be measured by thermal desorption (TDS) (annealing up to 700 °C).

In a first step, the hydrogen (deuterium) pick-up will be evaluated as a function of immersion time for the SoA (316L and Cantor). Based on these results, the charging time for the other 30 alloys will be determined. Important is to stay below melting point, to avoid contamination of the device. In this way, only the non-deeply trapped hydrogen will be estimated.

Standard sample size for TDS is 20×20×1 mm; for this project 12×10×5 mm will be used.



2.3 KPI 2.3: HNO_3 resistance (cast specimens)

Criteria

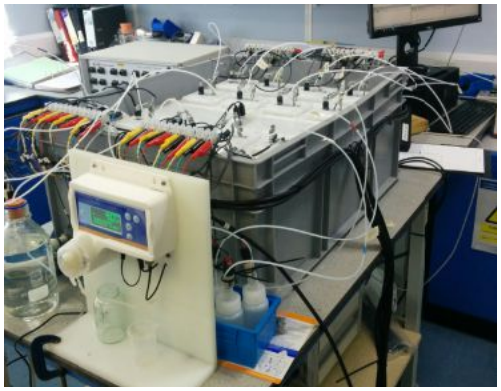
The targeted environment for the application of CCUS technology (i.e. PT1 in the FORGE project) is the Desulphurisation unit (De-SOx) of an oxy-combustion system applied to treat flue gases from clinker production[†]. The presence of CO_2, SO_x and NO_x in the flue gases leads to an extremely complex corrosive environment, often due to the development of acidic phases. The aim of this KPI is therefore to measure the corrosion rate of ~30 induction melted and ~6 arc-melted CCA specimens, in an environment simulating the corrosive conditions found in a De-SOx unit, however simplified to be able to test multiple specimens in a short amount of time as required by the timeline of the project. For this reason, electrochemical measurements of Linear Polarisation Resistance (LPR) in nitric acid (HNO_3) will be carried out for 1week at ambient temperature and pressure on each specimen to quantify the corrosion rate.

State of Art

Carbon steel pressure vessel with either 316L or 904L CRAs are often used as material solutions for the De-SOx unit. As the CRA material is in direct contact with the corrosive environment, this has been selected as state-of-the-art (SoA) material for this application. As 316L is generally more readily available than 904L it has been selected as the first SoA choice in the project, however 904L can also be tested if deemed necessary. 0.1 mm/y is the upper bound corrosion rate expected for 316L and 904L materials at ambient temperature and pressure and at HNO_3 concentrations <97 %[‡].

Test and Key Performance Indicators

The Linear Polarisation Resistance (LPR) test will be performed in accordance with ASTM G59 and ATSM G102, in a liquid solution containing 0.1 M HNO_3 (i.e. ~0.6%), at ambient pressure and temperature for 168 h (1-week). CCA specimens of 40×20×5 mm dimensions will be tested, although other geometries can also be used if necessary. Through the test, an accurate value of corrosion rate (mm/y) as a function of time can be calculated from the measured Polarisation Resistance (R_P). As the aim of these measurements is to generate training data points for the machine-learning model, corrosion rate performance is not of importance at this stage. A standard target corrosion rate <0.1 mm/y has nevertheless been defined as the upper boundary value for 316L stainless steel at <97 % HNO_3 and ambient conditions although, as explained, this will not be decisive in determining alloy selection for the following stages in the project.



[†] The cement industry is the biggest CO_2 emitter among the industries in the FORGE project, contributing to ~8% of global CO_2 emission. The majority of these emissions are generated by the calcination reaction in clinker production. Among the commercially ready CCUS technologies, oxy-combustion offers the most economical solution in terms of €/tonne of CO_2, while calcium looping, although promising, is still at research stage. Within the oxy-combustion cycle, the most corrosive conditions are found in the inlet ducting and pipework, compressor and De-SOx vessel immediately in contact with wet flue gases. Linings, either of flake-glass vinylester (FGV) or CRA are often employed for these components.

[‡] https://www.materials.sandvik/en-gb/materials-center/corrosion-tables/nitric-acid/

2.4 KPI 2.4: Nanohardness

Criteria

Hardness is the property important from an engineering point of view because it can be directly correlated to resistance to plastic deformation and wear by either friction, abrasion, or erosion. In the frame of the task, the nanoindentation tests will be employed to determine hardness of the PVD coatings.

In order to determine the accuracy of the machine learning model, the measured data will be compared to the predicted values.

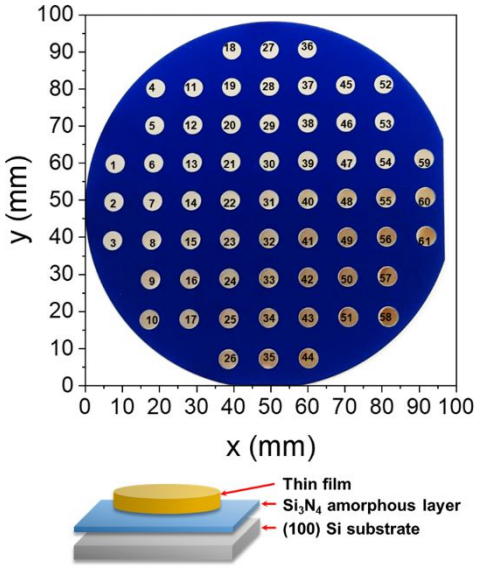
Hardness does not depend solely on the chemical composition. Other factors such as phase composition and texture (in the case of anisotropic materials) can also have a significant influence on the obtained properties. To understand and compare the mechanical properties of different CCAs produced in the form of gradient thin films, the nanoindentation and chemical composition (EDS / XRF) results will be supported by phase composition and texture (XRD) measurements. The risk with the measurements of PVD coatings, deposited on an oriented silicon wafer is that the wafer curvature may make it difficult to perform correct nanoindentation measurements. The PVD deposition with the mask will be performed to produce unconnected patches and thus reduce the stress in the thin film and the deflection of the wafer. Additionally, nanoindentation measurements will be carried out using the home-made vacuum holder which reduces wafer curvature.

State of Art

In the last decade, many CCAs have been developed and tested. As reference material, we have selected the Cantor alloy, on which the most rigorous and thorough investigations have been performed. The quinary $Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20}$ alloy was one of the first equiatomic HEAs reported to crystallize as a single-phase FCC solid solution. The hardness of the alloy in the as-cast state is 300 HV[§].

Test and Key Performance Indicators

The nanoindentation tests will be performed according to ISO 14577 standard. The test conditions will be adjusted according to the properties of the coating to ensure an indentation depth of ~10% of the coating thickness to avoid substrate effects. Measurements will be performed on the materials libraries, deposited in the form of ϕ5 × ~0.002 mm unconnected patches on an oriented 4-inch silicon wafer. Nanoindentation tests will be carried out using the Berkovich tip at room temperature with the strain rate in the range between 0.1 and 1 s^{-1}. The deviation from machine learning predicted hardness will be used as an indicator of the model quality.



[§] Cantor, B.; Chang, I. T. H.; Knight, P.; Vincent, A. J. B. Microstructural Development in Equiatomic Multicomponent Alloys. Mater. Sci. Eng. A 2004, 375–377, 213–218.

2.5 KPI 2.5: H_2 Charging

Criteria

Metals usually reveal a strength-ductility trade-off, i.e., a higher strength is usually accompanied with a lower ductility. Therefore, the strength change after hydrogen charging can be used to indicate whether the metal is embrittled by hydrogen charging. In consideration that yield strength is directly proportional to hardness, and the measurement of hardness of thin films is convenient and fast, the hardness variation after hydrogen charging has been selected as the KPI. In this project, nanoindentation tests will be performed on the as-deposited and hydrogen charged films, and the hardness will be compared. To obtain an accurate hardness, i.e., to reduce the substrate effect, the indentation depth should be kept within 10% of the film thickness, which is 200 nm for a 2 μm-thick film.

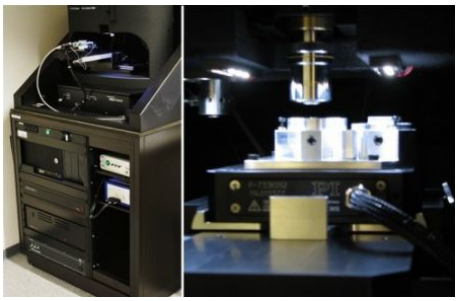
The risk of using hardness change as an indicator for hydrogen embrittlement is that hardness is not directly related brittleness or ductility, although harder metals often reveal lower ductility. Through indentation with depth much higher than 10% film thickness, such as 1.2 μm, the alloy films withstand large plastic strain and experience cracking. The number and length of the cracks can be checked in scanning electron microscope (SEM). The fewer number and shorter length of cracks corresponds to a higher plastic deformability of metals, and can be used to more accurately evaluate hydrogen embrittlement resistance. In order to ensure the efficiency and the completeness of the task, nanoindentations with higher depth such as 1.2 μm will only be performed on the samples that meet the KPI target value, and then the cracks will be checked in SEM.

State of Art

Among the immense compositional map of CCAs, the equiatomic CoCrFeMnNi CCA has attracted immense interest. The equiatomic CoCrFeMnNi CCA shows higher hydrogen embrittlement resistance than that of Inconel 718 alloy and AISI 310 stainless steel, which have long been used as benchmark materials for tolerance against hydrogen embrittlement[**]. With varying hydrogen content, the nanoindentation hardness of the CoCrFeMnNi CCA increases from 346 HV (uncharged) to 479 HV (1.15 wppm hydrogen) or 530 HV (3.00 wppm hydrogen)[††].

Test and Key Performance Indicators

Hydrogen will be introduced into the magnetron sputtered alloy films through electrochemical charging approach. The electrolyte used for hydrogen charging will be: 0.1 M NaOH+20 mg/L As_2O_3+deionized water. The hydrogen charging and nanoindentation testing will be performed at ambient temperature. The nanoindentation tests will be conducted in load-controlled mode in a nanoindenter (Agilent G200) with a Berkovich diamond tip. The strain rate will be controlled to be 0.1 s^{-1} upon loading. The indentation depth will be kept within 10 % of the film thickness, which is 200 nm for a 2 μm-thick film, to reduce the substrate effect. The nanoindentation tests will be performed on the as-deposited and hydrogen charged alloy films, and the hardness will be compared. The samples that achieved the KPI target values will be selected for nanoindentation tests with much higher depth such as 1.2 μm. The samples subjected to 1.2 μm indentation will be checked in SEM in order to more accurately evaluate the plastic deformability change after hydrogen charging.



[**] H. Luo, Z. Li, D. Raabe, Hydrogen enhances strength and ductility of an equiatomic high-entropy alloy, *Sci. Rep.* **7** (2017) 1–7.

[††] D. Wang, X. Lu, Y. Deng, D. Wan, Z. Li, A. Barnoush, Effect of hydrogen-induced surface steps on the nanomechanical behavior of a CoCrFeMnNi high-entropy alloy revealed by in-situ electrochemical nanoindentation, *Intermetallics* **114** (2019).

2.6 KPI 2.6: HNO_3 resistance (PVD patterns)

Criteria

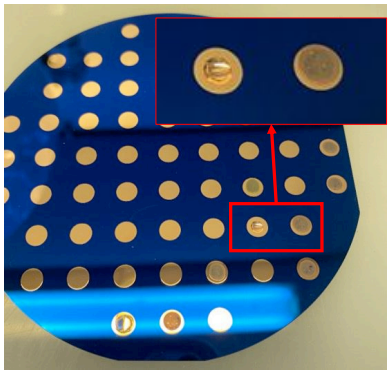
As already explained in the case of KPI 2.3, the targeted environment for the application of CCUS technology (i.e. PT1 in the FORGE project) is the Desulphurisation unit (De-SOx) of an oxy-combustion system applied to treat flue gases from clinker production[‡‡]. The presence of CO_2, SO_x and NO_x in the flue gases leads to an extremely complex corrosive environment, often due to the development of acidic phases. Unlike KPI2.3, the aim of this KPI is to measure the thickness loss of >300 Φ5 mm diameter PVD patterns generated for high-throughput CCA screening, in an environment simulating the corrosive conditions found in a De-SOx unit, however simplified to be able to test multiple specimens in a short amount of time as required by the timeline of the project. For this reason, a customised droplet exposure method has been designed specifically for the task. The method involves placing a droplet with a pre-determined volume containing HNO_3 on each of the PVD patterns for a specific amount of time. The exposure time will be determined by pre-tests on the actual CCA compositions once they will be predicted by the machine-learning model. The thickness loss, in mm/y is then determined by 3D morphological measurement performed by optical profilometry. Image analysis on optical and/or SEM micrographs of the corroded patterns could also be used should the 3D profilometry analysis be challenging.

State of Art

Carbon steel pressure vessel with either 316L or 904L CRAs are often used as material solutions for the De-SOx unit. As the CRA material is in direct contact with the corrosive environment, this has been selected as state-of-the-art (SoA) material for this application. As 316L is generally more readily available than 904L it has been selected as the first SoA choice in the project, however 904L can also be tested if deemed necessary. A corrosion rate <1 mm/y is expected for 316L and 904L at ambient temperature and pressure and at HNO_3 concentrations 98 %[§§]. This high concentration, although not representative of the actual field environment, is selected to provide accelerated corrosion conditions.

Test and Key Performance Indicators

This customised test is performed by placing 2.5 µl droplets of 98 % HNO_3 on top of each Φ5 mm diameter PVD pattern. The droplets will be maintained on the patterns for a total exposure time, which will be determined by pre-tests on the actual CCA compositions once they will be predicted by the machine-learning model. This time is expected to be between 5 and 20 min. The exposure will be performed at ambient temperature and pressure and at 100 % RH to avoid evaporation. A corrosion rate <1 mm/y is expected for 316L and 904L at ambient temperature and pressure and at HNO_3 concentrations 98 %. Thickness loss will be subsequently measured by means of 3D optical profilometry and/or optical/SEM microscopy as required.



[‡‡] The cement industry is the biggest CO_2 emitter among the industries in the FORGE project, contribut[illegible] of these emissions are generated by the calcination reaction in clinker production. Among the commercially ready CCUS technologies, oxy-combustion offers the most economical solution in terms of €/tonne of CO_2, while calcium looping, although promising, is still at research stage. Within the oxy-combustion cycle, the most corrosive conditions are found in the inlet ducting and pipework, compressor and De-SOx vessel immediately in contact with wet flue gases. Linings, either of flake-glass vinylester (FGV) or CRA are often employed for these components.

[§§] https://www.materials.sandvik/en-gb/materials-center/corrosion-tables/nitric-acid/

2.7 KPI 2.7: Composition Cost in CCA

Criteria

The selection of the elements to be used in the Machine Learning algorithm for the identification of the Compositionally Complex Alloys took into consideration multiple aspects, such as the specific performance targets, the processability within FORGE and by the industry, HSE consideration and of course Cost.

At early stage of development, it is difficult to establish a reasonable target, since the factors that will contribute to the final cost figure are too many, and including the deposition methods, the synthesis yield and the performance achieved.

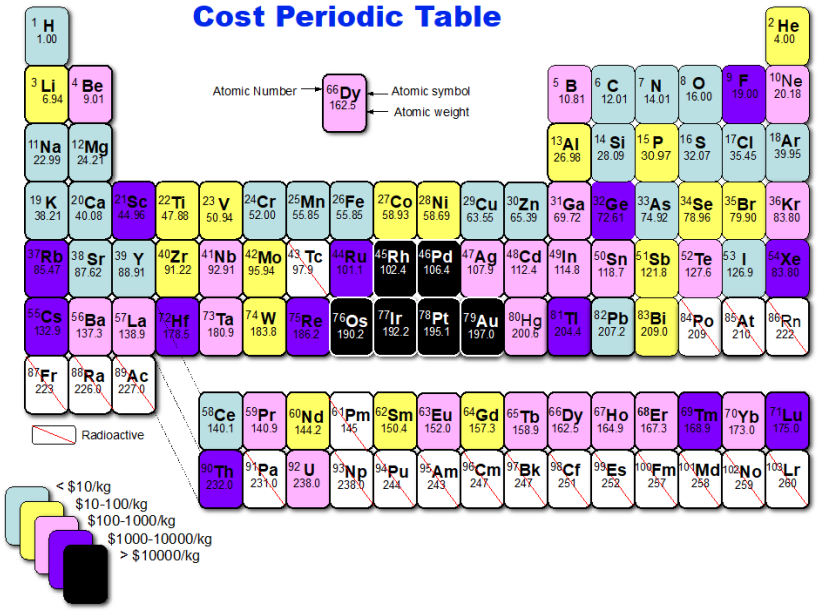
Notwithstanding this soon emerged the necessity to define a threshold that would discard from the ML model system, which is clearly heading toward an economical issue, such as systems with high amount of elements known to be expensive (i.e. Hf, Ta, Sc, Ge etc). On the other hand, to rely on common good sense might bias the early-stage selection of potentially good candidates.

State of Art

There is not a specific state of the art for this KPI, or a common reference value, since it would be closely related with the assumptions made to identify element cost and also with the period in which these costs are calculated.

Test and Key Performance Indicators

The identification of a reference cost of a Compositionally Complex Alloys can be straightforward within a defined framework. As a reference source of cost per kg of element we simply considered the data available from different sources, being the main source the German Mineral Resources Agency (DERA). The raw material costs are mostly considered as their stock prices; therefore, they are just indicative of the actual purchasing costs useful only for the purpose of ranking the different CCA and limit the ML model to addressable systems. The KPI reference value is set at 40€/kg for each composition. This value is calculated considering the amount of each component.



3 WORK PACKAGE 3

3.1 KPI 3.1 and 3.4: Porosity

Criteria

Pores in the coating can be a problem as they provide preferential diffusion paths for the permeation of corrosive gas species from the firing atmosphere to the refractory. The protective function of the coating would be decreased. Due to this the porosity and especially the open porosity must be minimised. Complete removal of porosity is not necessary as long as the residual pores are isolated. Therefore, a residual porosity of 5 % should be reached.

A reduction of porosity can be achieved by longer sintering times and higher sintering temperatures. However, the sintering conditions also influence the phase formation and the mechanical properties of the coating. Therefore, a trade-off with respect to porosity might have to be found. Additionally, the particle size of the starting material can be reduced. The higher surface leads to an increased sintering activity. Furthermore, a homogenous, high initial packing density reduces the risk of residual pores.

There are several known descriptions and standards for measuring the porosity of a material. One of the standard methods for determining the porosity together with the bulk density of a material is using a liquid (usually water) intrusion method which is also known as the Archimedes method. We will follow Method 1 of DIN EN 623-2, which is suitable for apparent porosity measurements greater than 1 %. This is also similar to Method A of ASTM D792 or ASTM B962 – 17 and ISO 1183.

As the liquid can only penetrate into the open pores, isolated pores are not measured. However, by using the bulk density (also a result of the Archimedes method) together with the density of the powdered material (e.g. determined by He-pycnometry of the powdered material) the total porosity can be calculated.

Alternatively, an optical method based on metallography could be applied as described in: ENV 1071-5.

State of Art

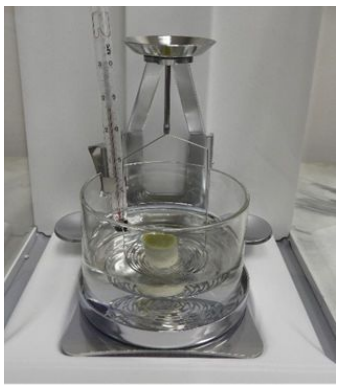
As the current refractory bricks do not have a coating, a porosity of a comparable standard coating is difficult to define.

Test and Key Performance Indicators

The determination of the porosity, which is one key parameter with respect to corrosion resistance at high temperatures (PT4) will be done using a water intrusion method known as the Archimedes method. We will follow Method 1 of DIN EN 623-2

The method requires the following steps:

1. Preparation of samples
2. Drying the test sample in an oven.
3. Determination of the mass of the dry test samples
4. Degassing the test sample under reduced pressure.
5. Immersing the test piece in water for filling the gas free pores
6. Determining the mass of the soaked test piece.
7. Determination of the apparent mass of the immersed test sample.
8. Determination of the apparent mass of the soaked test sample in air
9. Calculating Density and Porosity Values



A sample is weighed when immersed in distilled water and well soaked.

Except for the immersion step where the air inside the pores is eliminated due to reduced pressure, all steps are performed under normal conditions of temperature and pressure. Samples shall be cylindrical with a dimeter of about 5 mm and a thickness of 1-3 mm. Larger samples reduce the error but might contain larger amounts of closed pores. Other geometries are possible. The method does not depend on geometry.

It is a relatively fast and simple method that does not require exhaustive sample preparation.

The specimen will be prepared from both sol (T3.2, T3.4) and powder (T3.5) derived CCC ceramics and will also be used in the later development (T6.6).

3.2 KPI 3.2 and 3.5: Corrosion rate

Criteria

The main reason for the development of the CCC coatings is to increase the corrosion resistance of the refractory bricks in the furnace process, which allows longer service life of the furnace. Therefore, the corrosion rate should be as low as possible. The corrosion rate will be measured of both brick and sol-gel or powder-based coating materials, as well as on the coated refractory bricks. The target value of the corrosion rate of a coated refractory brick is a reduction to less than 50 % of the corrosion rate of the refractory bricks. For comparison, the quantity to be measured should be in thickness per furnace run (mm/run). However, in determining the corrosion rate, the risks and limitations arise that it may become difficult to quantify the corrosion rate exactly. Also, it is possible that the corrosion will take longer than the project FORGE will run. As a solution to this problem, a qualitative analysis could be performed on the behaviour of the coating.

State of Art

Currently the refractory bricks in the furnace do not have a corrosion resistant coating, which could be regarded as State of Art (SoA). However, since the corrosion rate of the refractory bricks is to be reduced, the corrosion rate of the not coated materials should be known and will be measured. Currently two refractory materials have been chosen for applying the coating: Refractory JM23 (low T), which consists of alumina and JM26 (high T), which consists of mullite. Currently the cost of the substrate is 500 €/m2. It has to be replaced every 5-6 years.

Test and Key Performance Indicators

The corrosion rate measurements will be performed in the tasks T3.2, T3.4 and T3.5 of WP3 and in the task T6.6 of WP6. It will be applied to the coating materials and the coated refractory bricks developed for the performance target PT4, which will be coated via a sol-gel or a powder-based route. For this purpose, the samples of the various coating materials are pressed into cylinders with a diameter of 5 mm and a thickness of about 1-3 mm. The tests will be carried out on sintered specimens, which will have smaller dimensions due to shrinkage. A more precise specification of these dimensions depends on the respective composition and cannot yet be made. Other geometries are also possible. The dimensions of the refractory bricks are 230×114×63 mm. However, other geometries can be used as well.

The sol derived and powder derived CCCs, as well as the coated refractory bricks will be exposed to the corrosive conditions of the gas burner at 900-1200 °C. The microstructural analysis after the customised corrosion exposure will be performed with optical microscopy and SEM in combination with energy-dispersive X-ray spectroscopy (EDS).

Optical microscope & Scanning electron microscope

3.3 KPI 3.3 and 3.6: CTE

Criteria

The coefficient of thermal expansion CTE describes the change of length of a material on heating. If the CTE of a coating and a substrate differ too much, stresses between the two materials will developed during temperature changes. Temperature changes can occur during start-up and cool-down of the furnace, temporal changes in the mode of operation or poor process control. Stresses can lead to crack formation, ablation and loss of the coating functionality. Additionally, pieces of coating can drop on the product and lead to defects.
The coefficient of thermal expansion is usually measured using dilatometers over a larger temperature range as it is not a linear property. The temperature range should encompass the real process conditions in the oven and will be set in our case from RT up to 1400 °C.
Usually push rod dilatometers are used. In special cases optical dilatometers give better results e.g. when the material under investigation softens or standard geometries cannot be prepared.
Different norms are described like DIN EN 821 "Determination of thermal expansion", DIN 51045-2 Testing of fired fine ceramic materials using the dilatometer method or ASTM E228. If the sample geometries that are necessary for push rod dilatometry cannot be prepared an alternative standard could be ISO 23458 or we use our in house developed thermo-optical measurement devices TOM.
In order to minimize the risk of stress development due to CTE-mismatch the difference in the CTE of two materials (substrate and coating) should be below 2 ppm/K with the CTE of the materials usually being in the range of 1-15 ppm/K.

State of Art

Currently the refractory bricks in the oven do not have a protective coating, which could be regarded as State of Art (SoA). However, as the difference in the CTE of the refractory and the coating will be the critical aspect, the substrate itself will be taken as standard. Currently two refractory materials have been chosen for applying the coating: Refractory JM23 (low T), JM26 (high T). The CTE of the refractory will be measured and compared to the values given by the supplier and used for comparison and goal.

Test and Key Performance Indicators

The thermal expansion of a material and the respective coefficient CTE is commonly measured by thermo-dilatometry, a technique in which a known dimension of a test specimen is measured under negligible applied force as a function of temperature while the specimen is subjected to a controlled-temperature program in a specified atmosphere. The measurement of the dimensional change can be done by direct mechanical measurement (Push-rod) or by optical techniques (e.g. TOM).
A push rod dilatometer consists of an oven, a sample holder and the unit for measuring data acquisition and evaluation. The standard sample geometry is a rod of 5 mm diameter (or 5 mm × 5 mm square) and 25 mm length. The cylinder faces have to be planar and parallel.
The quantitative determination of the change in dimension as a function of temperature is defined as the mean coefficient of linear thermal expansion. It is calculated as the ratio of a given change in length per unit length for a specimen for a specific change in temperature as follows:

$$\alpha = [(L_2 - L_1)/(T_2 - T_1)]/L_1$$

L1 and L2 = lengths of the test specimen at test temperatures T1 and T2, respectively, where T2 > T1.

With respect to PT4 the CTE of the refractory and both the sol-derived (T3.2, T3.4) and the powder derived (T3.5) CCC will be measured. Measurements are performed on sintered samples of the dimensions given above using a laboratory push rod dilatometry. As sample preparation is difficult only materials of high potential will be characterized. Deviations in length and size of the cross-sectional area are possible but faces should be plane parallel. The temperature range of the measurement will encompass the later oven conditions and range from RT to 1400 °C or the softening of the sample.

With respect to the predictability of machine learning the deviation of the predicted and measured value will be evaluated within T6.6.


Push-rod-Dilatometer and Thermo-optical measurement devices TOM

3.4 KPI 3.7: Composition Cost in CCC

Criteria

The initial pool of oxides for the development of Compositionally Complex Ceramics has been selected considering:

- Extent of use in industry,
- Known thermal and corrosive stability,
- Number and variety of compounds,
- Availability and cost.

The cost considerations havehave been made to keep the material development as close as possible to a direct industrial application. At the same time the KPI has been set high enough to allow a complete assessment of the possible oxide combinations that express aa high temperature resistance.

State of Art

There is not a specific state of the art for this KPI, or a common reference value, since it would be closely related with the assumptions made to identify element cost and also with the period in which these costs are calculated.

Test and Key Performance Indicators

The threshold value of 60 €/kg is considered an acceptable threshold, given the possible oxides composing the CCCs. The price estimated concerns the CCC coating via the powder route. The price depends largely on the composition (e.g. yttrium oxide is expensive). The price for the sol-gel-route would be 800 €/kg, but it should be noted that the price per kilogram refers to the pure coating material and not to the coated bricks. The coatings will be relatively thin, which means that not much material is required.

A strict application of this KPI might risk of excluding compositions potentially well performing, therefore if no, or too few, compositions are found within these limits, it can be considered to revise the threshold.

4 WORK PACKAGE 4

4.1 KPI 2.1, 3.1, 4: RMSE, PT1, PT2, PT3, PT4

Criteria

In WP2.1 and WP3.1, we develop Machine learning (ML) models for PT1, PT2, PT3, and PT4. Only PT3 is well studies for CCA in the literature.

All machine learning models require matrices to measure the accuracy of the trained model. We will be using ML models that use regression algorithms. Therefore, the deviation between test data and ML predictions is a measure of how well the model performs. A perfect model would have predictions that have zero deviation from the test data. Hence, we will use prediction error as the metric to validate ML model performance. The smaller the error, the better is the model. Also, it is necessary that we handle error symmetrically, where only absolute deviation from the measured data is important. Root mean Square Error (RMSE) fully fits this criterion. We will use RMSE as the metric to measure the accuracy of ML models for all PT values.

Our target RMSE for PT1 is ~0.1 mm/y, for PT2 ~10 HV, for PT3 < 50 HV, and for PT4 ~ 1e-6 /K. Accuracy of the ML models is highly dependent on the good training data. In case we have difficulty in generating enough data to reach high accuracy for PTs, we will use some data augmentation by interpolation and Monte Carlo resampling of measured data points.

Test and Key Performance Indicators

Measurement of error in predictions of any regression model is a standard practice in mathematics and machine learning. We will use Root Mean Square Error (RMSE) as the KPI for all the models in the FORGE project. RMSE is defined as,

$$RMSE = \sqrt{\sum_i^n \frac{(Y_i - y_i)^2}{n}}$$

Where Y_i are the measured data point (PT value) for a given parameter set x_i and y_i is the ML model predictions for the same x_i, n is the number of data points. RMSE compares prediction error of the model. Our goal is to minimize the RMSE value.

5 WORK PACKAGE 5

5.1 KPI 5.1: Powder Hall Flowability

Criteria

Powder Flowability is one of the key parameters that allows MBN to assess if a material is sprayable, the particle size ranges required for different thermal spray systems are not the same, the flowability measured with a Hall method can be a useful system for comparing different powders and give reliable feedbacks to the Machine Learning Model while, in the same time, provide indication for the downstream utilization of the powder.

The standard consists of measuring the time for 50 g of powder to pass through a funnel with a calibrated orifice. In order to compare powders with different compositions and densities, we have to consider the skeletal density and convert the results expected by the standard, in sec/g, to a comparable value in sec/cm^3.

This measurement is effective for free-flowing powders, but Non free-flowing powders can still be effective for the feeding system utilised many Thermal Spray equipment. Therefore, if considered too strictly, this KPI might rules out acceptable batches of powder. To mitigate this, if Non Free Flowing powders are proved effective in Thermal Spray, thenthen a different method can be used to assess their flowability: the Carney / Copley methods, which require larger samples and a dedicated reference map has to be defined.

State of Art

MBN has developed numerous powders for application in thermal spray, although none of these being a CCA and many of them being CerMet. It is not reasonable to consider as SoA reference for flowability a metal powder obtained with different techniques, since, especially for the flowability, the powders produce in MBN has a quite peculiar morphology that does not correlate directly with the major powder production techniques (Water Atomized and Gas Atomized). Therefore, a Tungsten-Nickel-Alloy has been chosen as reference, because it is sufficiently multinary, it is constituted by solely by metals and has been proved effective with multiple thermal spray techniques.

Test and Key Performance Indicators

This type of evaluation will be performed to assess powder batches in all the tasks of WP5. It will be applied to powders developed for PT1-2-3 and, although it is applicable to powder for PT4, it is not considered a Key Performance for PT4, in which the powders are dispersed in a slurry. The test will be performed by MBN using the material directly in its powder form and following the standard ASTM B213-03 "Method for Flow Rate of Metal Powders" which foresee the use of a calibrate funnel with orifice of 2.54 mm. The powder has to be properly dried to have consistent results, but the measurement is performed at normal temperature and pressure on 50 g of powder.

In order to convert the flowability value obtained with this technique, expressed in sec/g, the skeletal density of the powder has to be measured and utilised to convert flowability in sec/cm^3. This will be done following the ASTM B923-02 "Metal Powder Skeletal Density by Helium Pycnometry". A flowability value below 5 sec/cm^3 is considered an acceptable threshold for the powder in FORGE.

5.2 KPI 5.2: Powder Flowability – Hausner Ratio

Criteria

Hausner Ratio is a measuremeasure that can be used to predict the propensity of a given powder sample to be compressed, and that reflects the importance of inter-particulate interactions. These interactions are generally less significant for a free-flowing powder, for which the bulk and tapped densities will be relatively close in magnitude. Poorer flowing materials are characterized by the existence of larger interparticle interactions, so a greater difference between bulk and tapped densities is observed.

The Hausner ratio is standard practice in Powder Metallurgy and a value greater than 1.4, i.e. big differences between tap and bulk density, is considered to be an indication of poor flowability.

Since the feeding equipment utilised in FORGE differs for each Thermal Spray system, smaller values of Hausner Ratio can still indicate poorly flowable powder, for this reason we consider that an early round robin test on the different TS system will give information about the actual flowability issue and information to re-set the KPI threshold.

State of Art

Similarly, to the consideration done for KPI 5.1, a powder produced in MBN has been considered as reference for the state of the art. The W-Ni-Alloy chosen has a composition with more than three metal, and it is the closest one to a compositionally complex alloy. It would not be effective to have a reference in which the composition is partially constituted by ceramics, like for CerMet powders, or produce with different methodologies, like Gas Atomization, that will not be applied in FORGE.

The Hausner ratio of the reference materials is in the desired range, and the cost figures take into account similar production rate as those expected for FORGE.

Test and Key Performance Indicators

The evaluation of Hausner Ration will be applied to powders developed in tasks 5.1 5.2 and 5.3, and it is applicable to all the performance targets. MBN will perform the analysis on the powder following the ASTM standards for the evaluation of the bulk density (ASTM B212–99 "Method for Apparent Density of Free-Flowing Metal Powders Using the Hall Flowmeter Funnel") and the tap density (ASTM B527-93 "Method for Determination of Tap Density of Metallic Powders and Compounds"). These methods require to have properly dried powder and to be performed at normal pressure and temperature. In particular it is convenient to utilise ASTM B212-99 for the evaluation of the apparent density since it can be done in combination with the ASTM B213-03 for the evaluation of the flow rate.

6 WORK PACKAGE 6

6.1 KPI 6.1: Coating porosity (CCA)

Criteria

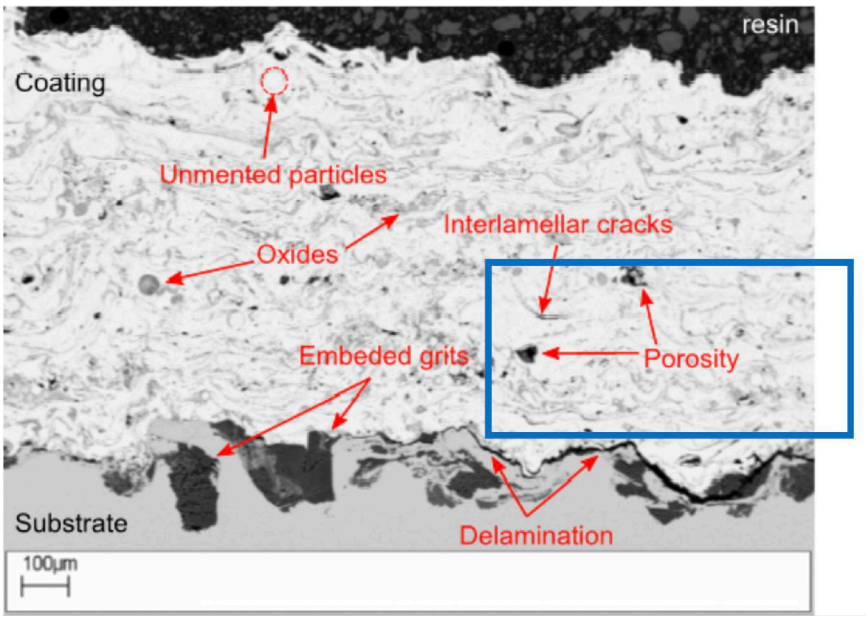
Porosity is one of the several defects found in coatings. In thermally sprayed (i.e. HVAF, HVOF) and cold sprayed coatings, porosity is generated by the dynamics of impact and flattening of incoming powder particles as they deform over previously deposited splats. In Laser Metal Deposited (LMD) coatings, porosity can be generated by either entrapped shielding or carrier gas or lack of fusion. For applications where the function of the coating is to act as a barrier to a corrosive liquid or gaseous medium, porosity can represent a preferential permeation path. A certain degree of porosity is often accepted in as-deposited coatings, especially for applications where thermal protection is an important factor. In the FORGE project, this is the case of the ceramic CCC coatings developed for PT4. In general, however, an excessive amount of pores (>~15 area% when measured via image analysis) is not recommended for any application as this will also worsen the mechanical properties (e.g. toughness) of the coating excessively. The aim of this KPI is therefore to minimise the porosity as much as possible. As the aim of the analysis at this stage is to compare different coating system, if multiple coatings are identified that fulfilfulfil the KPI, the selection will favour the systems with the minimum porosity among these. This KPI is applicable to all coatings deposited in WP6.

State of Art

Not applicable as the comparison is against uncoated materials.

Test and Key Performance Indicators

Metallographic examination will be performed on cross-sections taken from the as-deposited coatings. Coated substrates of dimensions 50×25×6 mm, coated on one side, can be processed, although different geometries can also be used if required. The cross-sections will be mounted in resin and polished to mirror finish. This will allow the coating microstructure to be revealed and possible defects identified. Porosity, in terms of area%, will be measured by image analysis and a <5 area% is considered acceptable for further coating testing, based on the experience in the consortium. This measurement is extremely sensitive to the sample preparation routine, settings (e.g. brightness/contrast) used while capturing the optical/SEM images and operator judgement while defining what constitutes porosity. It is therefore suggested that the measurement is performed by the same organisation/operator for all CCAs.



6.2 KPI 6.2: Coating cracks

Criteria

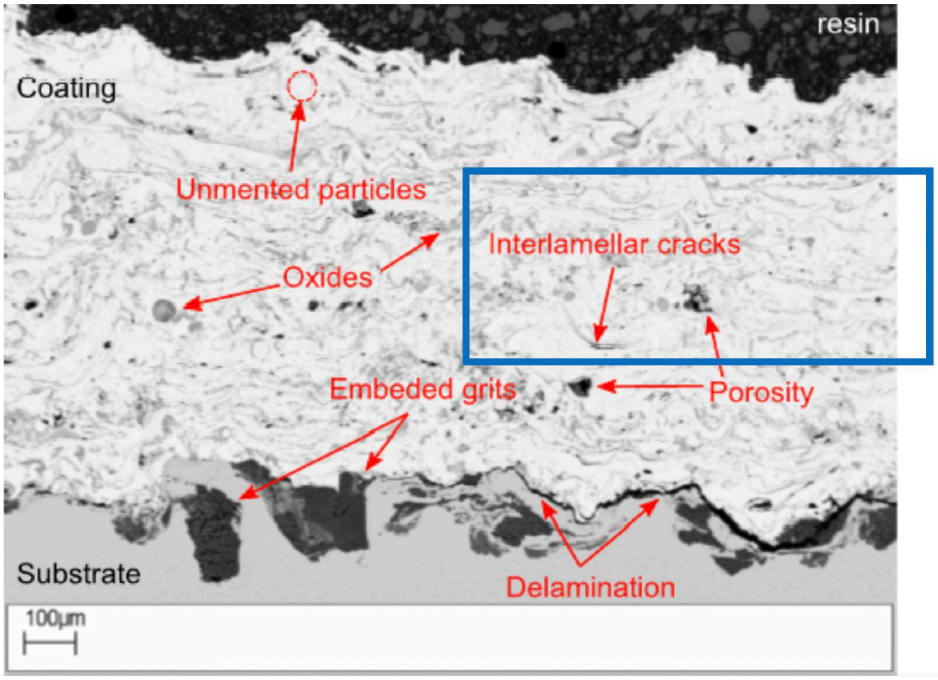
As for porosity, cracks are one of the several unwanted defects found in coatings. In thermally sprayed (i.e. HVAF, HVOF) and cold sprayed coatings, cracks can be either transverse (i.e. perpendicular to the substrate) or intra-lamellar (i.e. within the splat microstructure, generally in the vertical direction perpendicular to the substrate). In Laser Metal Deposited (LMD) coatings, cracks can be generally subdivided into cold cracks and hot cracks and are linked to several factors such as hydrogen, contaminants and thermodynamics of solidification. Cracks are unwanted in coatings as they reduce the toughness as well as representing preferential paths for liquid or gaseous contaminants. The aim of this KPI is therefore to observe no cracks in the as-deposited coatings. As the aim of the analysis at this stage is to compare different coating system, if all of the coatings are identified with a certain degree of cracking, selection priority will be given to the ones showing the lowest level of this quantity. This KPI is applicable to all coatings deposited in WP6.

State of Art

Not applicable as the comparison is against uncoated materials.

Test and Key Performance Indicators

Metallographic examination will be performed on cross-sections taken from the as-deposited coatings. Coated substrates of dimensions 50×25×6 mm, coated on one side, can be processed, although different geometries can also be used if required. The cross-sections will be mounted in resin and polished to mirror finish. This will allow the coating microstructure to be revealed and possible defects identified. Cracks will be counted and their extension evaluated. The coating(s) showing the lowest amount of cracks will be selected for further testing in the project. This measurement is extremely sensitive to the sample preparation routine, settings (e.g. brightness/contrast) used while capturing the optical/SEM images and operator judgement while defining what constitutes porosity. It is therefore suggested that the measurement is performed by the same organisation/operator for all CCAs.



6.3 KPI 6.3: Coating/substrate interfacial delamination

Criteria

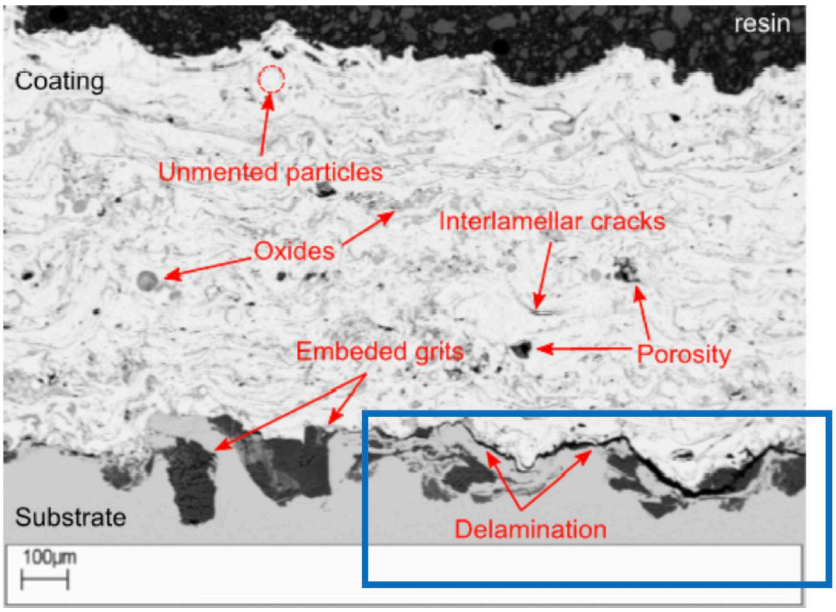
As for the previous two KPIs in this work package, interfacial delamination is one of the several unwanted defects found in coatings. In coatings, delamination is observed as one or more long cracks running parallel to the coating/substrate interface. Development of delamination is linked to tensile stresses developing during coating deposition. These are linked to differences in coefficient of Young's modulus and coefficient of thermal expansion (CTE) between coating and substrate material, as well as temperature variations during deposition. Interfacial delamination cannot be accepted in the as-deposited coatings and therefore coatings showing such a feature will be discarded from further analysis in the project. This KPI is applicable to all coatings deposited in WP6.

State of Art

Not applicable as the comparison is against uncoated materials.

Test and Key Performance Indicators

Metallographic examination will be performed on cross-sections taken from the as-deposited coatings. Coated substrates of dimensions 50×25×6 mm, coated on one side, can be processed, although different geometries can also be used if required. The cross-sections will be mounted in resin and polished to mirror finish. This will allow the coating microstructure to be revealed and possible defects identified. Interfacial delamination, if present, will be identified and only the coatings not presenting this feature will be selected for further testing. This type of measurement is extremely sensitive to the sample preparation routine, settings (e.g. brightness/contrast) used while capturing the optical/SEM images, and operator judgement while defining what constitutes porosity. It is therefore suggested that the measurement is performed by the same organisation/operator for all CCAs.



6.4 KPI 6.4: Erosion wear

Criteria

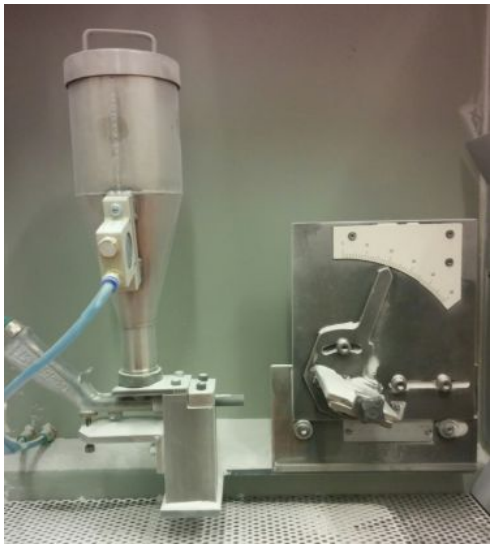
An excessive presence of defects (i.e. porosity, cracks, etc.) is expected to have a direct impact into the mechanical properties, specifically toughness, of the coating. Measuring the mechanical performance of the coatings deposited by means of different techniques can therefore be employed to further verify the absence of defects as well their intrinsic wear resistance (relevant for PT3). This test will therefore be employed as a KPI stage gate only for the CCA material defined for PT3 at this stage. Among the methodologies for measuring wear resistance, erosion wear testing based on ASTM G76 represents a flexible way, which can allow for all of the different coating types produced in the project to be analysed. The test involves determining coating material loss, in terms of g/min, by impingement of gas-entrapped solid particles. Chemistry and morphology of the solid particles, carrier gas pressure, exposure time and relative orientation of the coated substrate in respect to the nozzle can be varied in the test.

State of Art

The state-of-the-art (SoA) material selected for PT3 throughout the project is HB450 (UNS S45000) steel. As the performance of this material against the erosion wear test is currently not known, the value will be measured during the project.

Test and Key Performance Indicators

The test will be performed by using 20mesh white alumina as solid particles and air as carrier gas. The exposure will be carried out for 140s with coated coupons inclined 20° with respect to the horizontal plane. Weight loss measurement will be performed by weighting the coupons via analytical balance before and after the test. Coupons dimensions must be 40x40x6mm (inclusive of coating), with coating applied on one side only. No other geometry can be tested, as this will affect the validity of the comparison between different systems. The specified KPI value of <0.071 g/min, valid only for the CCA material related to PT3, has been selected as previously measured on a HVOF Cr3C2-NiCr cermet coating at TWI Ltd. For all of the other CCA coatings in WP6, this test will be employed to compare, for the same material and deposition technique, which set of deposition parameters give rise to the coating with higher toughness. This test will therefore be employed as a KPI stage gate only for the CCA material defined for PT3 at this stage.



Erosion test on coating by alumina sand blasting

6.5 KPI 6.5: Coating porosity (CCC)

Criteria

Pores in the coating can be a problem as they provide preferential diffusion paths for the permeation of corrosive gas species from the firing atmosphere to the refractory. The protective function of the coating would be decreased. Due to this the porosity and especially the open porosity must be minimised. Complete removal of porosity is not necessary as long as the residual pores are isolated. Therefore, a residual porosity of 5% should be reached.

A reduction of porosity can be achieved by longer sintering times and higher sintering temperatures. However, the sintering conditions also have an influence on the phase formation and the mechanical properties of the coating. Therefore, a trade-off with respect to porosity might have to be found. Additionally, the particle size of the starting material can be reduced. The higher surface leads to an increased sintering activity. Furthermore, a homogenous, high initial packing density reduces the risk of residual pores.

There are several known descriptions and standards for measuring the porosity of a material. One of the standard methods for determining the porosity together with the bulk density of a material is using a liquid (usually water) intrusion method which is also known as the Archimedes method. We will follow Method 1 of DIN EN 623-2, which is suitable for apparent porosity measurements greater than 1%. This is also similar to Method A of ASTM D792 or ASTM B962 – 17 and ISO 1183.

As the liquid can only penetrate into the open pores, isolated pores are not measured. However, by using the bulk density (also a results of the Archimedes method) together with the density of the powdered material (e.g. determined by He-pycnometry of the powdered material) the total porosity can be calculated.

Alternatively, an optical method based on metallography could be applied as described in: ENV 1071-5.

State of Art

As the current refractory bricks do not have a coating, a porosity of a comparable standard coating is difficult to define.

Test and Key Performance Indicators

The determination of the porosity, which is one key parameter with respect to corrosion resistance at high temperatures (PT4) will be done using a water intrusion method known as the Archimedes method. We will follow Method 1 of DIN EN 623-2

The method requires the following steps:

1. Preparation of samples
2. Drying the test sample in an oven.
3. Determination of the mass of the dry test samples
4. Degassing the test sample under reduced pressure.
5. Immersing the test piece in water for filling the gas free pores
6. Determining the mass of the soaked test piece.
7. Determination of the apparent mass of the immersed test sample.
8. Determination of the apparent mass of the soaked test sample in air
9. Calculating Density and Porosity Values

Except for the immersion step where the air inside the pores is eliminated due to reduced pressure, all steps are performed under normal conditions of temperature and pressure. Samples shall be cylindrical with a dimeter of about 5 mm and a thickness of 1-3 mm. Larger samples reduce the error but might contain larger amounts of closed pores. Other geometries are possible. The method does not depend on geometry.

It is a relatively fast and simple method which does not require exhaustive sample preparation.

The specimen will be prepared from both sol (T3.2, T3.4) and powder (T3.5) derived CCC ceramics and will also be used in the later development (T6.6).

6.6 KPI 6.6: Corrosion rate

Criteria

The main reason for the development of the CCC coatings is to increase the corrosion resistance of the refractory bricks in the furnace process, which allows longer service life of the furnace. Therefore, the corrosion rate should be as low as possible. The corrosion rate will be measured of both brick and sol-gel or powder-based coating materials, as well as on the coated refractory bricks. The target value of the corrosion rate of a final coated refractory brick is a reduction to less than 50 % of the corrosion rate of the refractory bricks. For comparison, the quantity to be measured should be in length per furnace run (mm/run). However, in determining the corrosion rate, the risks and limitations arise that it may become difficult to quantify the corrosion rate exactly. Also, it is possible that the determination of the corrosion rate will take longer than the project FORGE will run. As a solution to this problem, a qualitative analysis could be performed on the behaviour of the coating.

State of Art

Currently the refractory bricks in the furnace do not have a corrosion resistant coating, which could be regarded as State of Art (SoA). However, since the corrosion rate of the refractory bricks is to be reduced, the corrosion rate of the not coated materials should be known and will be measured. Currently two refractory materials have been chosen for applying the coating: Refractory JM23 (low T), which consists of alumina and JM26 (high T), which consists of mullite. Currently the cost of the substrate is 500 €/m2. It has to be replaced every 5-6 years.

Test and Key Performance Indicators

The corrosion rate measurements will be performed in the tasks T3.2, T3.4 and T3.5 of WP3 and in the task T6.6 of WP6. It will be applied to the coating materials and the coated refractory bricks developed for the performance target PT4, which will be coated via a sol-gel or a powder-based route. For this purpose, the samples of the various coating materials are pressed into cylinders with a diameter of 5 mm and a thickness of about 1-3 mm. The tests will be carried out on sintered specimens, which will have smaller dimensions due to shrinkage. A more precise specification of these dimensions depends on the respective composition and cannot yet be made. Other geometries are also possible. The dimensions of the refractory bricks are 230×114×63× mm. However, other geometries can be used as well.

The sol derived and powder derived CCCs, as well as the coated refractory bricks will be exposed to the corrosive conditions of the gas burner at 900-1200 °C. The microstructural analysis after the customised corrosion exposure will be performed with optical microscopy and SEM in combination with energy-dispersive X-ray spectroscopy (EDS).

6.7 KPI 6.7: CTE

Criteria

The coefficient of thermal expansion CTE describes the change of length of a material on heating. If the CTE of a coating and a substrate differ too much, stresses between the two materials will developed during temperature changes. Temperature changes can occur during start-up and cool-down of the furnace, temporal changes in the mode of operation or poor process control. Stresses can lead to crack formation, ablation and loss of the coating functionality. Additionally, pieces of coating can drop on the product and lead to defects.
The coefficient of thermal expansion is usually measured using dilatometers over a larger temperature range as it is not a linear property. The temperature range should encompass the real process conditions in the oven and will be set in our case from RT up to 1400°C.
Usually push rod dilatometers are used. In special cases optical dilatometers give better results e.g. when the material under investigation softens or standard geometries cannot be prepared.
Different norms are described like DIN EN 821 "Determination of thermal expansion", DIN 51045-2 Testing of fired fine ceramic materials using the dilatometer method or ASTM E228. If the sample geometries that are necessary for push rod dilatometry cannot be prepared an alternative standard could be ISO 23458 or we use our in house developed thermo-optical measurement devices TOM.
In order to minimize the risk of stress development due to CTE-mismatch the difference in the CTE of two materials (substrate and coating) should be below 2 ppm/K with the CTE of the materials usually being in the range of 1-15 ppm/K.

State of Art

Currently the refractory bricks in the oven do not have a protective coating, which could be regarded as State of Art SoA. However, as the difference in the CTE of the refractory and the coating will be the critical aspect, the substrate itself will be taken as standard. Currently two refractory materials have been chosen for applying the coating: Refractory JM23 (low T), JM26 (high T). The CTE of the refractory will be measured and compared to the values given by the supplier and used for comparison and goal. Currently the cost of the substrate is 500 €/m2. It has to be replaced every 5-6 years.

Test and Key Performance Indicators

The thermal expansion of a material and the respective coefficient CTE is commonly measured by thermo-dilatometry, a technique in which a known dimension of a test specimen is measured under negligible applied force as a function of temperature while the specimen is subjected to a controlled-temperature program in a specified atmosphere. The measurement of the dimensional change can be done by direct mechanical measurement (Push-rod) or by optical techniques (e.g. TOM).
A push rod dilatometer consists of an oven, a sample holder and the unit for measuring data acquisition and evaluation. The standard sample geometry is a rod of 5 mm diameter (or 5mm*5mm square) and 25 mm length. The cylinder faces have to be planar and parallel.
The quantitative determination of the change in dimension as a function of temperature is defined as the mean coefficient of linear thermal expansion. It is calculated as the ratio of a given change in length per unit length for a specimen for a specific change in temperature as follows:

$$\alpha = [(L_2 - L_1)/(T_2 - T_1)]/L_1$$

L1 and L2 = lengths of the test specimen at test temperatures T1 and T2, respectively, where T2 > T1.

With respect to PT4 the CTE of the refractory and both the sol-derived (T3.2, T3.4) and the powder derived (T3.5) CCC will be measured. Measurements are performed on sintered samples of the dimensions given above using a laboratory push rod dilatometry. As sample preparation is difficult only materials of high potential will be characterized. Deviations in length and size of the cross-sectional area are possible but faces should be plane parallel. The temperature range of the measurement will encompass the later oven conditions and range from RT to 1400 °C or the softening of the sample.

With respect to the predictability of machine learning the deviation of the predicted and measured value will be evaluated within T6.6.

7 WORK PACKAGE 7

7.1 KPI 7.1: HNO_3 resistance (Coatings)

Criteria

As explained in the KPIs related to WP2, the targeted environment for the application of CCUS technology (i.e. PT1 in the FORGE project) is the Desulphurisation unit (De-SOx) of an oxy-combustion system applied to treat flue gases from clinker production[***]. As the aim of this work package is to down-select the best coatings among the systems prepared in WP6, in this KPI the corrosion rate of 4 coatings of the CCA developed for PT1 will be measured in an environment simulating the corrosive conditions found in a De-SOx unit. As the number of specimens is now reduced compared to the similar KPIs in WP2, tests in more aggressive conditions can be now performed. This will involve higher exposure times, temperature and pressure compared to WP2. Exposure tests (no electrochemical analysis) will be performed in accordance with ASTM G1, G157 and G31.

State of Art

Carbon steel pressure vessel with either 316L or 904L CRAs are often used as material solutions for the De-SOx unit. As the CRA material is in direct contact with the corrosive environment, this has been selected as state-of-the-art (SoA) material for this application. As 316L is generally more readily available than 904L it has been selected as the first SoA choice in the project, however 904L can also be tested if deemed necessary. A corrosion rate <1 mm/y is expected for 316L and 904L at ambient temperature and pressure and at HNO_3 concentrations 98 %[†††], although the actual value will be measured during the project. This high concentration, although not representative of the actual field environment, is selected to provide accelerated corrosion conditions.

Test and Key Performance Indicators

The exposure test will be performed in a glass vessel in accordance with ASTM G1, G157 and G31. Coated coupons of approximate dimension 40×40×6 mm (although this can vary) will be held on an ad-hoc designed sample holder made of a material not susceptible to the testing environment. 98 % HNO_3, 50 °C temperature, 1-8 bar pressure and exposure times of 1 month will be employed for the tests. Corrosion rate measurement post-exposure will be performed by metallographic examination of the exposed specimens' cross-sections. The corrosion rate (in mm/y) will be measured by analysing the portion of coating thickness affected by the corrosive environment. This could be in the form of depth of permeated electrolyte (for porous coatings), thickness reduction or scale thickness. The measurement is non-trivial as it requires interpretation, unlike electrochemical measurement where a value of corrosion rate is returned. The KPI value will be adjusted compared to the <1 mm/y value currently selected, by measuring the corrosion rate of the SoA material at the conditions specified for the test.

[***] The cement industry is the biggest CO_2 emitter among the industries in the FORGE project, contributing to ~8% of global CO_2 emission. The majority of these emissions are generated by the calcination reaction in clinker production. Among the commercially ready CCUS technologies, oxy-combustion offers the most economical solution in terms of €/tonne of CO_2, while calcium looping, although promising, is still at research stage. Within the oxy-combustion cycle, the most corrosive conditions are found in the inlet ducting and pipework, compressor and De-SOx vessel immediately in contact with wet flue gases. Linings, either of flake-glass vinylester (FGV) or CRA are often employed for these components.

[†††] https://www.materials.sandvik/en-gb/materials-center/corrosion-tables/nitric-acid/

7.2 KPI 7.2: H_2 pick-up

Criteria

As in WP2, the H_2 content after charging will be measured on coated samples. The less H_2 diffused into the material, the less it is susceptible to cracking. The main difference with WP 2 is the type of samples (coated samples here versus bulk samples in WP2) and the way of charging the samples.

Charging here will be done by high pressure gaseous charging (of hydrogen, not deuterium) instead of using a solution, based on heavy water and measurement via hot extraction instead of thermal desorption. Target is to have the same (or a lower) hydrogen content than for the SoA material, or at least see a significant reduction of the amount of hydrogen as compared to the uncoated sample.

The factor coated samples further complicates the interpretation of results, as it will be difficult to separate the H-content form the coating and the substrate. All edges of the sample need to be coated. An alternative could be to use a permeation technique, applied on substrate only and substrate+coating, although this method is not fully operational yet at ARC.

State of Art

The SoA material considered is stainless steel 316L (UNS31603), which has a cost of approximately 6 USD/kg. The value for the KPI for this material remains to be determined, under the exact same conditions as the material under study.

Test and Key Performance Indicators

Testing of 4 coated samples, the uncoated substrate and the SoA material, via charging with hydrogen in the autoclave at 200 bar, followed by hot extraction (i.e. below 900 °C). This technique measures the amount of (diffusible) hydrogen in wt ppm. Standard geometry is 20×20×1 mm, although higher thicknesses (2-3 mm) are also possible; 15×15×1 mm is the minimum surface area. Important is that the sample is coated on both sides and on the edges. 3 samples per material are requested to estimate scatter. Target is to have the same (or a lower) hydrogen content than for the SoA material, or at least see a significant reduction of the amount of hydrogen as compared to the uncoated sample.

Disk rupture test

7.3 KPI 7.3: Resistance to abrasive wear

Criteria

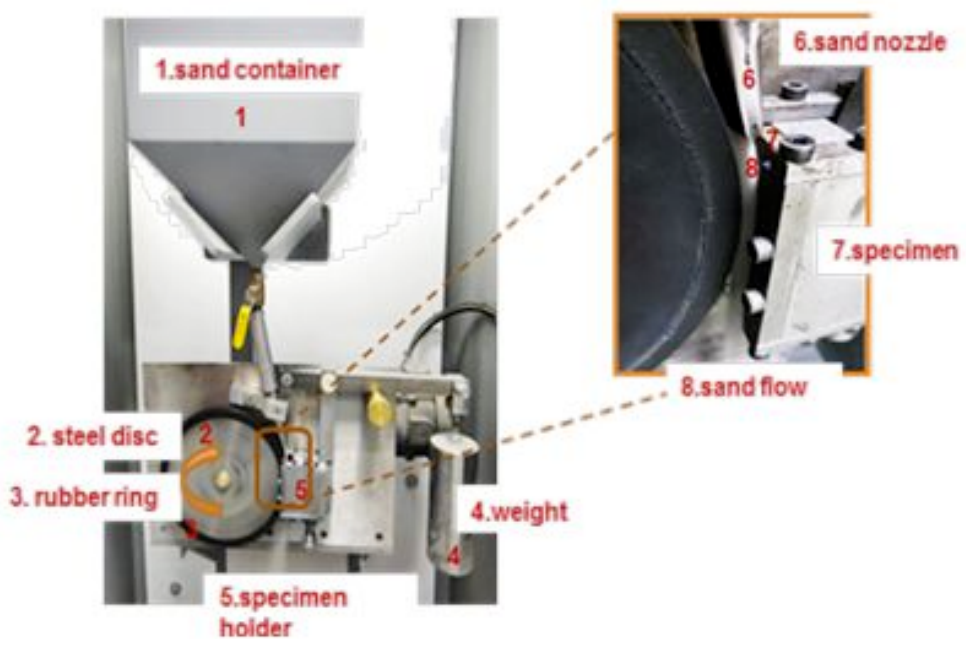
Here the wear of the coated samples will be tested by measuring the volume loss (in mm³) via sliding wear (ASTM G65). In ASTM G65, a procedure C exists for coated materials. The typical procedure applied at ARC is procedure B for bulk materials. The KPI target value via this procedure B is 80 mm³ but needs to be determined in procedure C (which will be lower). Procedure B can likely not be applied, as the coating might be worn off too quickly and wear of the uncoated substrate will be measured. It is also suggested to measure the wear rate/volume loss of the uncoated substrate (which is not necessarily the SoA material).

State of Art

The SoA material for this application is the steel HB450, with a hardness of 500 HV and a volume loss in procedure B of 80 mm³; value in procedure C to be evaluated. The cost of this SoA is about 1 USD/kg.

Test and Key Performance Indicators

Measurement of the volume loss of 6 samples in total: 4 coated samples, the uncoated substrate and the SoA material, via **ASTM G65 procedure C**. Standard sample size is 75×25×5 mm; thickness can vary between 3 and 10 mm. Lower thickness is not allowed due to risk of wearing through the sample. At least 5-6 samples per material should be foreseen, to allow sufficient repetitions.



7.4 KPI 7.4: Cracking after high temperature and thermal cycling

Criteria

Refractories used at industrial kilns degrades over time due to corrosion. The deterioration, induced by the corrosion, leads to formation of cracks, which appear in the refractory bricks and other structural refractory elements. Hence, a certain number of cracks can be expected in the coatings after exposure. These are an indication of microstructural modifications occurring in the material This must be avoided otherwise the debris dethatching from the refractory brick can fall on tiles being fired, compromising their quality.

The corrosion, cause of the development of cracks, will be indirectly measured as (number of cracks/mm of interface). It could happen that the testing time is too short to cause cracks in the samples located in the kiln. If this happens, the exposure time will be increased. Another risk associated with this KPI is that not all the crack appearing in the refractory bricks might be caused by corrosion problems, in which case specific control reference have to be implemented.

The indicator will be measured for both bare refractory brick sample and CCC-coated brick sample, to compare the performance of the new coating with the standard solution without any coating.

State of Art

The refractory materials used in continuous roller kilns for firing ceramic tiles are mainly refractory bricks and other structural pieces used for building the dome. These materials will be the substrate where the CCC coating will be applied and tested.

The state of the art of this KPI will be measured in the uncoated refractory substrate, after its exposure to the kiln conditions during the testing time in WP7. This reference value will be used to get the performance of the CCC coatings tested by comparison between the coated samples with the uncoated substrate.

The comparison between the number of cracks developed in refractory without coating and in the coated samples with the news CCC coatings developed, will guide the selection of the more appropriate coating for this application.

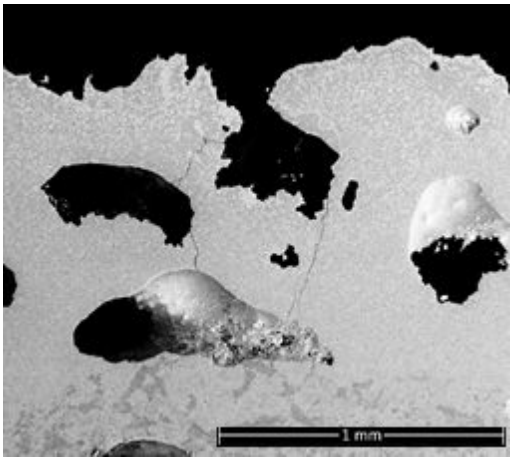
Test and Key Performance Indicators

The selected substrates will be coated with the new developed CCC coatings, which will be slurries, easy to apply on the surface of the samples.

The samples will be placed inside the kiln, on the floor, in several locations, each one at different temperature. After the testing time, both the uncoated refractory used as a reference and the coated samples will be removed from the industrial kiln and analysed.

Cracking in the coated and uncoated refractories after being exposed to high temperature will be evaluated by SEM. Four test pieces will be cut from each refractory tested (50×50×60 mm). They will be mounted, in cross-section, in an epoxy resin and polished to a 1µm finish using a diamond suspension. Then, they will be observed and photographed with the backscattered electron signal of a field-emission gun environmental scanning electron microscope (SEM). For each test piece, in the glassy layer formed on the surface of the refractories, the number of cracks perpendicular to the surface will be counted and expressed per unit interface length. The results will be averaged for the four test pieces.

Cracks on the deteriorated surface of refractories, cross-section view.



7.5 KPI 7.5: Interfacial delamination after high temperature and thermal cycling Criteria

Refractories used at industrial kilns degrades over time due to corrosion. The corrosion determines interfacial delamination/s that appears in the refractory bricks and other structural refractory elements. Hence, interfacial delamination/s can be expected in the coatings after exposure. These are an indication of microstructural modifications occurring in the material, that must be avoided.

The degradation, referred to the development of interfacial delamination/s, will be measured as (length of interfacial delamination/s/mm of interface). It could happen that the testing time is too short to cause interfacial delamination/s in the samples located in the kiln. If this happens, exposure time will be increased.

The indicator will be measured for both bare refractory brick sample and CCC-coated brick sample, to compare the performance of the new coating with the standard solution without any coating.

State of Art

The refractory materials used in continuous roller kilns for firing ceramic tiles are mainly refractory bricks and other structural pieces used for building the dome. These materials will be the substrate where the CCC coating will be applied and tested.

The state of the art of this KPI will be measured in the uncoated refractory substrate, after its exposure to the kiln conditions during the testing time in WP7. This reference value will be used to get the performance of the CCC coatings tested by comparison between the coated samples with the uncoated substrate.

The comparison between the length of the delamination/s per unit length of interface developed in refractory without coating and in the coated samples with the news CCC coatings developed, will guide the selection of the more appropriate coating for this application.

Test and Key Performance Indicators

The selected substrates will be coated with the new developed CCC coatings, which will be slurries, easy to apply on the surface of the samples.

The samples will be placed inside the kiln, on the floor, in several locations, each one at different temperature. After the testing time, both the uncoated refractory used as a reference and the coated samples will be removed from the industrial kiln and analysed.

Interfacial delamination/s in the coated and uncoated refractories after being exposed to high temperature will be evaluated by SEM. Four test pieces will be cut from each refractory tested (50×50×60 mm). They will be mounted, in cross-section, in an epoxy resin and polished to a 1µm finish using a diamond suspension. Then, they will be observed and photographed with the backscattered electron signal of a field-emission gun environmental scanning electron microscope (SEM). For each test piece, in the glassy layer formed on the surface of the refractories and in a region close to it, the length of the delamination/s (crack/s parallel to the surface) will be measured and expressed per unit interface length. The results will be averaged for the four test pieces.

Damaged refractory, showing delamination.

7.6 KPI 7.6: Corrosion after high temperature and thermal cycling

Criteria

Refractories used at industrial kilns degrades over time due to corrosion. The deterioration could be the development of a glassy layer on the refractory surface. This is an indication of microstructural modifications occurring in the material, that must be avoided.

The degradation, induced by the corrosion, can be measured considering the extent of development of a glassy layer on the refractory surface, thic can be measured by relating the depth of material deteriorated (measured from the exposed surface to the harsh ambient) to the exposure time, and the units will be mm per year (mm/y), i.e., by determining the corrosion rate. It could happen that the testing time is too short to cause cracks in the samples located in the kiln. If this happens, exposure time will be increased.

The indicator will be measured for both bare refractory brick sample and CCC-coated brick sample, to compare the performance of the new coating in preventing the corrosion, hence the degradation, with the standard solution without any coating.

State of Art

The refractory materials used in continuous roller kilns for firing ceramic tiles are mainly refractory bricks and other structural pieces used for building the dome. These materials will be the substrate where the CCC coating will be applied and tested.

The state of the art of this KPI will be measured in the uncoated refractory substrate, after its exposure to the kiln conditions during the testing time in WP7. This reference value will be used to get the performance of the CCC coatings tested by comparison between the coated samples with the uncoated substrate.

The comparison between the corrosion rate of the refractory without coating and in the coated samples with the news CCC coatings developed, will guide the selection of the more appropriate coating for this application.

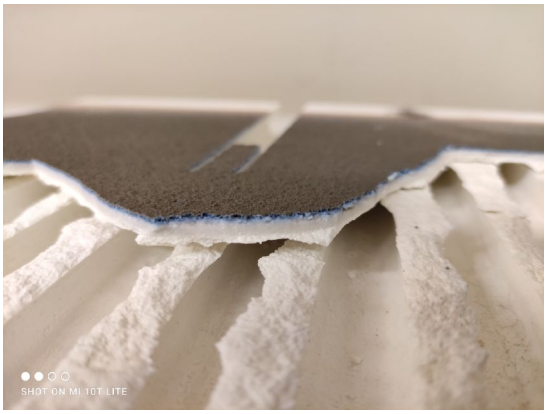
Test and Key Performance Indicators

The selected substrates will be coated with the new developed CCC coatings, which will be slurries, easy to apply on the surface of the samples.

The samples will be placed inside the kiln, on the floor, in several locations, each one at different temperature. After the testing time, both the uncoated refractory used as a reference and the coated samples will be removed from the industrial kiln and analysed.

Corrosion in the coated and uncoated refractories after being exposed to high temperature will be evaluated by SEM-EDS. Four test pieces will be cut from each refractory tested (50×50×60 mm). They will be mounted, in cross-section, in an epoxy resin and polished to a 1 µm finish using a diamond suspension. Then, they will be observed and photographed with the backscattered electron signal of a field-emission gun environmental scanning electron microscope (SEM). For each test piece, thickness of the glassy layer formed on the surface of the refractories will be measured and characterized and expressed per year of exposition (corrosion rate). The results will be averaged for the four test pieces.

Deteriorated piece of refractory located at the dome of an industrial kiln.



7.7 KPI 7.7: Sliding wear

Criteria

The mechanism of wear that mainly contribute to the premature degradation of the extrusion dies is sliding wear.

Analysis will be applied to the samples made of extrusion die materials. Sliding wear analysis will be done by pinball on disk technique, in order to check if the FORGE solution increased the wear resistance or not. It is expected to enhance wear characteristics of the materials by 20% Therefore selected KPI value is 0.8 when SoA wear resistance divided to CCA wear resistance value.

The only and minor risk is selection of wrong parameters and wrong sample preparation. If the risk occurs, then the test must be repeated.

State of Art

The state of the art is represented by the current used technologies: the materials of extrusion dies are 1.2344 (AISI H13) for open profile die and nitrided 1.2367 (X38CrMoV5-3) for solid profile dies on both material a nitride coating is applied by PDV. Dimensions of the SoA components are 330 mm diameter and 115 mm thickness for open profile die and 280 mm diameter and 185 mm thickness for solid profile die. Average values will be measured within the FORGE project by subcontracting tests to the university. 100 €/piece cost has been determined to run sliding wear test.

Test and Key Performance Indicators

Sliding wear will be evaluated via the pin/ball on disc test with respect to ASTM G99. 50 mm diameter and 5 mm thick disc preparation are expected for sample preparation. Test will be carried out at room temperature and high temperatures (extrusion die temperature) which also be validated after QForm simulations. High temperature values are expected to be between 450-550 °C.

Pin on disk test

8 WORK PACKAGE 8

8.1 KPI 8.1: Emission intensity

Criteria

The emission intensity is the key parameter allowing Tailorlux to characterise the luminescent properties of a tracer in terms of detectability and sensor readability. A high signal in the characteristic spectral features is necessary for the definition of a measurement reference for the custom measuring sensorics.

An altogether absolute measurement of the luminescent intensity is a complex procedure and not possible with the facility available at Tailorlux. Therefore, a comparison measurement with the emission intensity of a comparison standard, namely "Reference tracer 010-000013" is routinely performed.

The suitability of this comparative analysis with "Reference tracer 010-000013" as a benchmark has already been proven and is established as a standard for the majority of Tailorlux applications due to the very high emission intensity.

A pre-characterization in optical reflection and excitation allows the definition of the correct values for the test variables. The newly synthesized markers are measured at their respective excitation maximum and the intensity of their main emission is related to the maximum peak of the basic marker 010-000013 under 365 nm excitation.

All comparative optical fluorescence measurements are designed for powders, the synthesized samples must therefore be reduced in powder form by grinding. Synthesis resulting in hard sintered samples are excluded from the portfolio and the synthesis routes/parameters are adjusted accordingly.

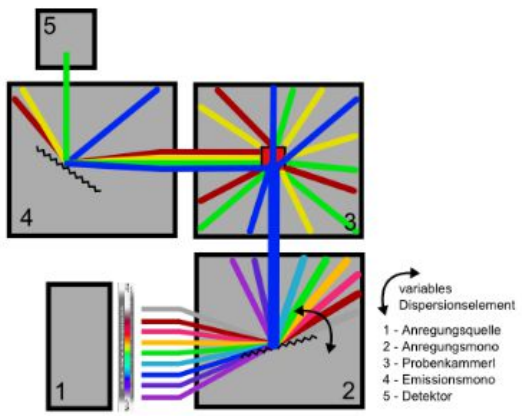
In case of spectrometer failure, spare parts such as a new excitation lamp are available. In case of unexpectedly long repair time of the measurement equipment, transitional measurements will be ordered/performed at Münster UAS.

State of Art

The base marker 010-000013 is used as an internal standard for the comparability of the newly developed fluorescent markers. The material is already available in powder form and all samples originate from a single homogenous batch. Thus, it shows a good target value for device-readable intensities of markers.

Test and Key Performance Indicators

The evaluation will be performed for all synthesised tracers in WP8.1. The test will be performed at Tailorlux on an Edinburgh Instruments FSL920 fluorescence spectrometer at room temperature conditions. An ozone-free 450 W xenon discharge lamp will be used as the excitation source. Furthermore, the spectrometer is equipped with a TMS300 excitation and emission monochromator in Czerny-Turner optics and an integrating sphere coated with spektralon as a sample chamber. A single photon counting photomultiplier R2658P from Hamamatsu in a refrigerated enclosure at -18 °C is used for detection. The setup of the fluorescence spectrometer is shown schematically in the following diagram.



The measurement parameters for determining the KPI Emission Intensity are summarized in table form:

	Ref. tracer 010-000013	**FORGE tracer**
Excitation wavelength	365 nm	Emission Maximum
Excitation and emission slit	10 nm/ 1 nm	10 nm/ 1 nm
Optical step	1 nm	1 nm
Haltezeit	0,4 s	0,4 s
Grating	500 nm blazed	500 nm blazed
Measuring range	400nm -600 nm Filter 395nm 550 nm-800 nm Filter 550 nm	400nm -600 nm Filter 395nm 550 nm-800 nm Filter 550 nm

The emission spectra are measured by exciting the sample at a specific wavelength (excitation wavelengths from table) and tuning the emission monochromator to record the energy distribution of the emission in the desired wavelength range. For intensity comparison at different emission wavelengths, it is important to apply the internal correction function which corrects the wavelength-dependent intensity deviations by comparing the emission spectrum measured with the instrument in question and the actual emission spectrum of a calibrated lamp.

From the two measured and corrected emissivity spectra, the count rates at maximum intensity are related: IProbe/IReference. This value in the unit % represents the performance indicator "emission intensity".

8.2 KPI 8.2: Emission quenching temperatures

Criteria

The thermal quenching behaviour of taggants is a known feature of luminescent materials and depends on plenty factors e.g. the kind of the crystal structure hosting luminescent centres and/or concentration of luminescence centres. Although the decomposition of the crystal structure is rather impossible at temperatures <1600 °C, repetitive exposure of taggants to higher or lower temperatures may influence their optical properties, via thermal activation of defects or some migration processes.

As the main application of the tracer+cca smart coatings is foreseen in specimens exposed either to constant high temperature or high temperature cycles it is important to characterise the raw material in this fashion, even if the probability of lowering the emission intensity upon cycled thermal treatment is rather low. Any changes in temperature dependent emission intensity should therefore be tested to ensure the functionality of the composite.

Two distinct values will be defined:

- TQ_{50} is the temperature where the 50 % of emission intensity is lost
- TQ_{95} is the temperature where the 95 % of emission intensity is lost

Reversibility of the quenched state will be defined in KPI 8.3

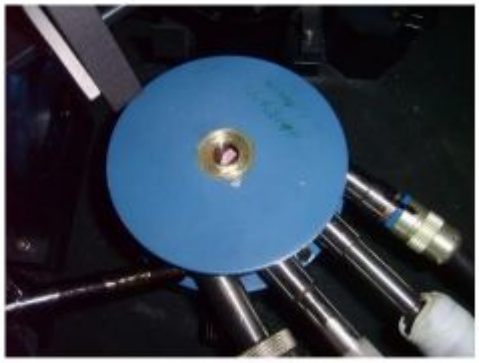
State of Art

Similarly, to what was reported in KPI 8.1 the marker 010-000013 will be used as reference for the emission intensity of the tracer at room temperature conditions. The only difference between the two techniques lies within the different temperature in the measurements.

Test and Key Performance Indicators

In addition to the standard spectrometric test conditions reported in KPI 8.1 the following will be performed:

For recording thermal quenching (TQ) curves a cryostat "MicrostatN" from Oxford Instruments is introduced in the above described spectrometer equipment. Measurements are carried out from 77 to 500 K in 50 K steps. For TQ measurements in the range from 350 to 800 K an in-house constructed sample holder is used. This holder comprises a heater located underneath the cavity for the sample and is made of corundum ceramic. The heater comprises an ISA®-CHROM60 filament with a diameter of 0.5 mm. The housing of the sample holder is actively cooled by flowing water.



MicrostatN (Oxford Instruments)

800 K-Heater

Plotting the intensity over the temperature provides a curve that shows the thermal behaviour of the taggant. By fitting the curve with a Fermi-Dirac or Boltzmann fit the TQ_{50} and TQ_{95} can be derived.

8.3 KPI 8.3: Optical emission at extreme conditions

Criteria

Luminescent centers in taggants are sensitive to exposure to molecural oxygen or so called forming gas (5-10%H_2/95-90%N_2). This sensitivity is specific for the luminescence activators which can undergo an oxidation process (Eu^{2+} to Eu^{3+}) or reduction (Cr^{4+} to Cr^{3+}). This usually results in a significant change in the luminescent properties, often worsening them.

If the oxidation/reduction reaction is completely performed then no detection of the taggant is possible anymore.

Another detrimental influence of prolonged exposure to a gas atmosphere might be the introduction of defects into the tracer structure, further quenching the luminescent properties of the taggant and thus their detectability.

In addition, the change in valence of the luminescent activators in presence of an oxdative or reductive atmosphere can be accelerated at higher temperature.

Long exposure to high temperature or extreme temperature cycling can also affect the luminescence of the material, especially in combination with the forming gas.

The selection of the atmospheres strongly depends on the future application of the smart coatings, nevertheless the tests should be at least performed in presence of molecular O_2, CO; H_2, H_2N_2.

Target values for the KPI are the retention of 70 % of the luminescence of the untreated material in the case of thermal cycles and the retention of 20 % of the luminescence of the untreated material in the case of the combination of thermal cycles with gas exposure.

The number of thermal cycles leading to <70 % luminescence will not be considered a KPI per se, but still reported as a useful auxiliary variable.

State of Art

The analysis is performed similarly to what was reported for KPI 8.1 and 8.2, only this time the reference for luminescence has to be taken from the non-degraded luminescent pigment. The base reference for the non-degraded luminescent pigment remains the marker 010-000013 at standard conditions.

Test and Key Performance Indicators

In addition to the standard spectrometric test conditions reported in KPI 8.1 and the temperature variable conditions reported in KPI 8.2 the following will be performed:

Thermal cycling in air:

Rather than a measure in the high temperature state, the sample hosted in the same experimental setup as KPI 8.2 will be heated to the TQ_{50} and TQ_{95} temperature then let naturally cool back to room temperature (22 °C). The luminescent intensity will be measured accordingly to the method described in KPI 8.1 with reference to an aliquot of the same sample kept at room temperature. The procedure will be repeated in cycles with N between 5 and 10.

Exposure to forming gas at room and high temperature:

Aliquots from samples produced in WP1 will be set in a reaction oven and subject to gas flow of H_2 O_2 CO H_2N_2 at rates between 50 and 150 l per hour. Samples can be exposed to the gas for a time tbd. The temperature can be set at values up to 1800 K. The procedure will be repeated in cycles with N between 5 and 10.

8.4 KPI 8.4: Sensor performance in WHR environment

Criteria

Spectrometric measurements in the high temperature range pose a significant challenge both on the instrumental and the data consistency aspect.

Independently from the emission power of a pure luminescent pigment or a pigment + cca composite under the harsh condition, the signal must first be effectively collected and the receiving instrument must be able to properly operate under the desired conditions.

In the specific case of spectrometry and related electronics this is extremely challenging when considering continuous operating temperatures in the order of 500°C, as this implies a very high thermal-dependent signal fluctuation as well as an elevated risk of component breakdown. When considering a bench or laboratory environment this can relatively easily be mitigated via dedicated accessory equipment, which become cumbersome when considering a field solution sensor like the one proposed in D8.4.

For the developed field sensor, the efficiency should be at least 80% of the laboratory analogous when performing room temperature measurements of fluorescent pigment with reference with the standard.

Considering the possibility of temperature-induced λ-shift, the spectral features such as characteristic peaks and bands of the tracer must be recognizable in a ±5nm environment. In the worst-case scenario of the direct measurement in high temperature status the intensity of the spectral features must be at least 10% of what measured in standard conditions.

Mitigation measures for the aforementioned issues with regards to a field sensor are:

- The decoupling of the sensor unit from the measuring unit (i.e. via a fiber patch cable)
- The identification and continuous measurement in a region of less extreme conditions, yet with a significant enough experimental information
- The planning and definition of measurement standards for components at near room temperature in the case, for example, of routine shutdown/maintenance cycles.

State of Art

Tailorlux has developed several product lines of spectrometric sensors, including units for heavy duty 24/7 measuring and reporting to be installed in production lines in the textile and automotive industry. These are the Tailor-Scan; Tailor-Spec and Inline-Sensor. The specific operative conditions of the cement industry represent a big step in requirements, as Tailorlux hasn´t tackled such a challenge yet. Nevertheless, it is well known that fluorescent spectrometry at high temperature is physically and instrumentally possible in controlled laboratory conditions. Many tools, like dedicated fibrefibre patch cables and optical components for high-temperature measurements are readily available on the market for a reasonable price (<500 EUR) decking operative temperatures up to 280 °C.

Test and Key Performance Indicators

The test will be performed via a custom-built sensor unit, whose exact characteristics heavily depend on the tracer downdown selected as candidate in WP8.1 to WP8.3. An appropriate spectrometric unit will be selected for the construction with regards to wavelength range configuration, dynamic range, optical resolution, signal/noise ratio, entrance slit, stray light, exposure time range, detector type.

In addition, all parts and accessories, including lenses, filters, beam splitters, slits, LED, laser units, fibrefibre patch cables will be selected as much as possible among OEM off-the-shelf available spares.

The testing conditions for the sensor performance will be included between samples/parts at room temperature which have undergone exposure to the WHR environment as well as samples/parts currently in operation at max. 500 °C. As the geometry and the exact composition of the plant site for the analysis is still to be determined, no preliminary considerations can be done about the precise field test conditions.

8.5 KPI 8.5: Adhesion strength

Criteria

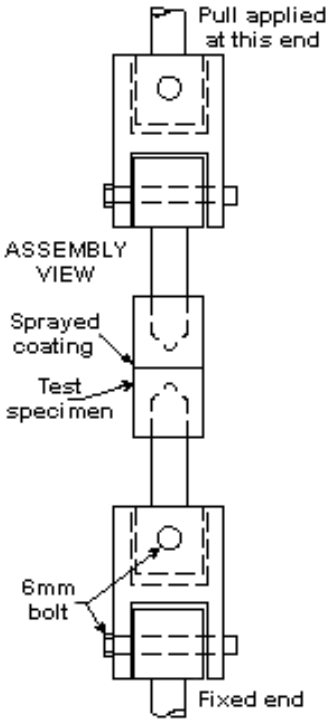
The presence of an additional phase in the coating selected for PT3, i.e. the taggant, will alter its microstructure and chemistry, and in turn its mechanical properties of the coating compared to the CCA-only system. Ideally, the CCA + taggant system will have comparable or better adhesion strength than the CCA-only one. This is particularly important for thermally sprayed (i.e. HVAF, HVOF) and cold sprayed coatings, particularly as the coatings are not metallurgically bonded to the substrate and therefore adhesion is very dependent on the conditions of the surface prior to coating deposition. The most common approach to determine coating adhesion is to measure the tensile load needed to detach the coating from the substrate, as described by the ASTM standard C633. In this KPI therefore, the adhesion strength of CCA+taggant coating will be compared to the one of CCA-only coating.

State of Art

The state-of-the-art (SoA) system selected for this KPI is the coating made of CCA-only. It's adhesion strength will be measured during the project and compared to the one measured on the CCA+taggant coating.

Test and Key Performance Indicators

The tensile adhesion strength test will be performed according to ASTM C633 standard. For the test, CCA and CCA+taggant coatings will be deposited onto the face of a 1in. diameter cylindrical specimen, which will be then bonded onto the face of another (uncoated) cylindrical specimen of the same diameter by high strength epoxy resin. The tensile strength of the coating results from dividing maximum load applied at failure by the cross-sectional area. The bond strength is given if failure occurs at the coating substrate interface. The cohesive strength of the coating is given if the failure occurs entirely within the coating. Often, for mostmost coatings, failure will occur in the epoxy adhesive. This gives an upper bond strength as measured by this method of about 80 MPa, *i.e.* the tensile strength of the adhesive. An alternative approach is to measure the adhesion, on flat specimens, in accordance with ASTM D4541 by means of a portable pull-off adhesion tester. In this case, a micro-hydraulic system is used to apply a tensile load to a cylindrical test piece adhesively bonded to the coating surface.



9 WORK PACKAGE 9

9.1 KPI 9.1: Resistance to corrosion in CO_2 rich environment

Criteria

As explained in the KPIs related to PT1, the targeted environment for the application of CCUS technology is the Desulphurisation unit (De-SOx) of an oxy-combustion system applied to treat flue gases from clinker production[‡‡‡]. As the aim of this work package is to test the down-selected coating from WP7, in this KPI the corrosion rate of 1 coating of the CCA developed for PT1 will be measured in an environment as close as possible to the one found in a De-SOx unit. As only one sample, together with the comparison SoA material is tested here, tests in more aggressive conditions can be now performed. For this reason, electrochemical measurements of Linear Polarisation Resistance (LPR) in nitric acid (HNO_3) and other species present in the final environment (i.e. H_2O, O_2, H_2SO_4, HCl) will be carried out for up to 3 months at higher temperatures and pressure than what tested previously in the project.

State of Art

Carbon steel pressure vessel with either 316L or 904L CRAs are often used as material solutions for the De-SOx unit. As the CRA material is in direct contact with the corrosive environment, this has been selected as state-of-the-art (SoA) material for this application. As 316L is generally more readily available than 904L it has been selected as the first SoA choice in the project, however 904L can also be tested if deemed necessary. A corrosion rate <1 mm/y is expected for 316L and 904L at ambient temperature and pressure and at HNO_3 concentrations 98%[§§§], although the actual value will be measured during the project. This high concentration, although not representative of the actual field environment, is selected to provide accelerated corrosion conditions.

Test and Key Performance Indicators

The Linear Polarisation Resistance (LPR) test will be performed, in glass autoclaves, in accordance with ASTM G59 and ATSM G102, in a liquid solution containing HNO_3, and other species present in the final environment: O_2, H_2SO_4, HCl. The exact concentration selected for each species will be determined during the project after discussions with cement and CCUS manufacturers. Temperatures between 40 and 90 °C, pressures between 1-8bar and exposures times of up to 3 months will be employed for the test. Coated specimens of Φ25.4×5 mm dimensions will be tested, although other geometries can also be used if necessary. Through the test, an accurate value of corrosion rate (mm/y) as a function of time is from the measured Polarisation Resistance (R_P). The KPI value will be adjusted compared to the <1mm/y value currently selected, by measuring the corrosion rate of the SoA material at the conditions specified for the test.

[‡‡‡] The cement industry is the biggest CO_2 emitter among the industries in the FORGE project, contributing to ~8% of global CO_2 emission. The majority of these emissions are generated by the calcination reaction in clinker production. Among the commercially ready CCUS technologies, oxy-combustion offers the most economical solution in terms of €/tonne of CO_2, while calcium looping, although promising, is still at research stage. Within the oxy-combustion cycle, the most corrosive conditions are found in the inlet ducting and pipework, compressor and De-SOx vessel immediately in contact with wet flue gases. Linings, either of flake-glass vinylester (FGV) or CRA are often employed for these components.

[§§§] https://www.materials.sandvik/en-gb/materials-center/corrosion-tables/nitric-acid/

9.2 KPI 9.2: Resistance to H_2 pressure (disc rupture)

Criteria

In a disc rupture test, a ratio of pressures at which disc samples break under pure He and (pure) H_2 pHe/pH_2. Preferably, this ratio is as close to 1 as possible. A typical value measured for the substrate material (with high strength) is 2-3; for lower strength stainless steels (316L/304), the value is between 1 and 1.5, but they are not strong enough for the target application. Therefore, the target value for this application is a ratio <2.

There are two main risks connected to this technique:

- Samples that are too thick cannot be measured
- Cracking of the coating could lead to H_2 entry into the high strength substrate material (which is known to be very vulnerable to hydrogen embrittlement)

The latter risk could be mitigated by performing interrupted tests in He to verify if cracks form in the coating, limit the pressure increase rate or perform isopressure tests below the cracking limit.

State of Art

State of the art material is stainless steel 316L (UNS S31603 – cost: ~6 USD/kg), for which the pressure ratio pHe/pH_2 lies in the range 1-1.5, but as mentioned above does not offer the target strength.

Substrate material will be a high strength steel with a YS ~1200MPa, for which the ratio is 2-3.

Test and Key Performance Indicators

In the disc rupture test (ISO 11114-4), the test piece (a disc of 75 mm diameter and 0.75 mm thickness) is subjected to a constantly increasing gas pressure, starting at 1 bar and going up to 1000 bar, at a rate between 0.1 and 100 bar/min. The test is first performed in Helium, afterwards in H_2 gas. The ratio of the gas pressures at which it breaks in eacheach atmosphere is determined.

One type of coated samples will be tested (coating technique to be selected based on the results from WP7). Important is that the coating is applied only on one side, roughness should be less than 1 µm and flatness should not deflect more than 0.1 mm.

Although the standard thickness is 0.75 mm, thicknesses in the range of 0.5 to 2 mm should be possible.

9.3 KPI 9.3: Resistance to H_2 pressure (permeation)

Criteria

A second aspect to evaluate the resistance to H_2 pressure of the CCA coating is to evaluate the permeation rate/ diffusion coefficient (cm^2/s) to go through the coating into the substrate. The diffusion coefficient for the SoA material is 3×10^{11} cm^2/s. The target is not to be higher than this reference value.

The objective is to measure this diffusion coefficient in a high-pressure gaseous environment. However, this methodology is currently under development at ARC. Alternatively, permeation tests in aqueous environment or in H2S are fully operational and could be applied.

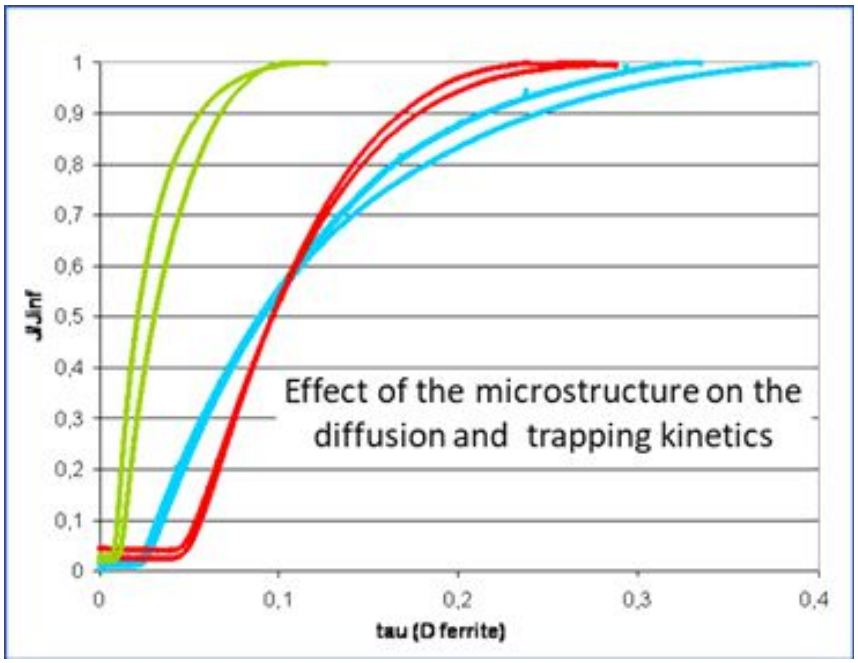
State of Art

State of the art material is stainless steel 316L (UNS S31603 – cost: ~6 USD/kg), for which the diffusion coefficient is 3×10^{11} cm^2/s.

Test and Key Performance Indicators

For this H_2 permeation technique, one type of coated samples will be tested (coating technique to be selected based on the results from WP7). Important is that the coating is applied only on one side.

However, as mentioned above, the methodology is currently still under development and the test conditions or geometries have not been finalized yet.



9.4 KPI 9.4: Resistance to impact wear

Criteria

The target of the impeller tumbler test is to evaluate the wear rate of one coated material versus SoA, under different conditions than WP7, i.e. under impact wear instead of sliding wear.

The wear rate (in mm/year) evaluated from the test is standard compared to a reference material (in this case the same as our SoA). The target is to reach minimum 20% improvement, preferably 50%, as compared to the SoA, so the KPI value (wear rate – CCA/ wear rate – SoA) should be >1.2, preferably >1.5.

Possible risks to the test are:

- accurate precision of sample dimensions is highly required
- coating on all sides, including the edges
- delamination of the coating
- effect of the base material cannot be accurately accounted for

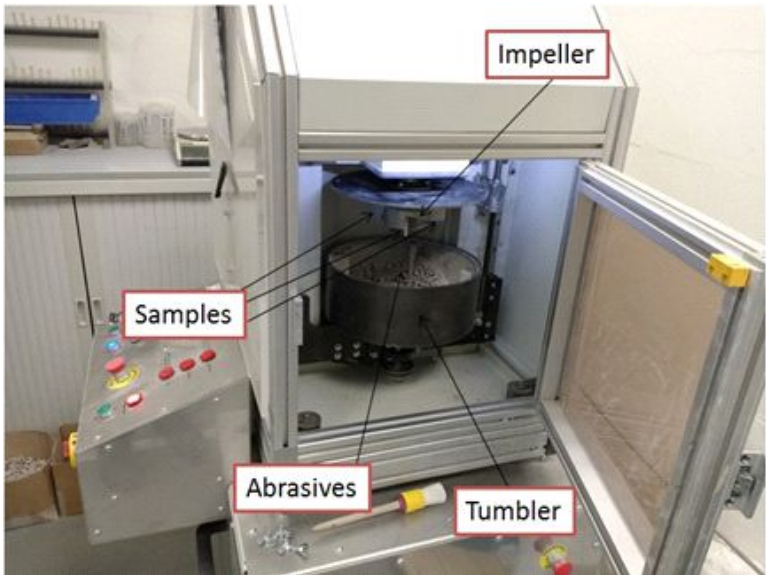
A proper substrate material should be chosen (which is not the same as our SoA) and the bare substrate will be tested as well.

State of Art

The SoA material is the wear resistant steel grade HB450 (cost: ~1 USD/kg), which is also the reference material used in the impeller tumbler test, over which the results are always normalized.

Test and Key Performance Indicators

The impeller tumbler test is a non-standard test used to measure the resistance to impact abrasion wear. During the test, an impeller rotates inside a rotating tumbler, filled with abrasives. Three samples, of which one is the reference sample, are attached to the impeller. As both the impeller and the tumbler rotate, the abrasives are being moved around and impact onto the samples. The total test duration is 3 hours; abrasives are refreshed several times during the test. The abrasives are chosen based on the final application. Sample dimensions are 65×25×5 mm. One coated and uncoated material will be tested, together with the reference HB450. At least 5-6 samples/material are required to ensure good reproducibility.



9.5 KPI 9.5 Wear resistance of WHR duct and damper blades

Criteria

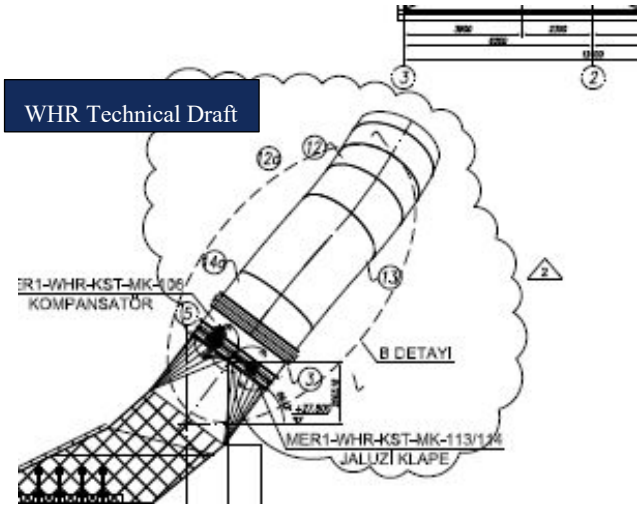
Waste Heat Recovery (WHR) ideally have a thickness of 8 mm in the gas ducts, and itit is expected not to fall below 5 mm. The thickness measurement is made with the standard thickness measuring device and based on the result, the relevant decision is made either to change the component or not. The frequency of change is normally every 5 years. The highest temperature the system is exposed to is 650 °C, and, although this is a short-term exposure, ST37- 2 material can bebe deformed, especially if high temperatures above 450 °C are used. In this case the material loses its properties and shortens the replacement period. The pipe has a circular cross section. The application area has a circular cross section.

State of Art

In the application area, temperature resistance of the material should be at least 450 °C and its thickness should be 8 mm. The material used is Standard steel ST37-2. This is preferred because of its affordable cost. The increase in the thickness of the material will require the project to consider new static calculations due to the weight increases. A continuous measurement cannot be made on the field because it is a hot zone, therefore measurements are made after the relevant area has been cooled down during the revision period.

Test and Key Performance Indicators

Temperature resistance should be at least 450 °C, materials with high resistance to abrasion and thermal effects should be used. Depending on the increased weight of applications that will increase the current weight, the risk and application process should be evaluated.



WHR Technical Draft

WHR

9.6 KPI 9.6 coating resistance on WHR damper blades

Criteria

InI the WHR,, the damper blade system is also a key component that undergoes premature wear due to the erosion by hot clinker dust. Here the FORGE coating, applied to the blades, can be exposed to the real environment and its erosion monitored. Since the blades are maintained annually due to their rapid wear, it is expected that by means of ultrasonic testing the erosion can be determined during regular maintenance operation of the component.

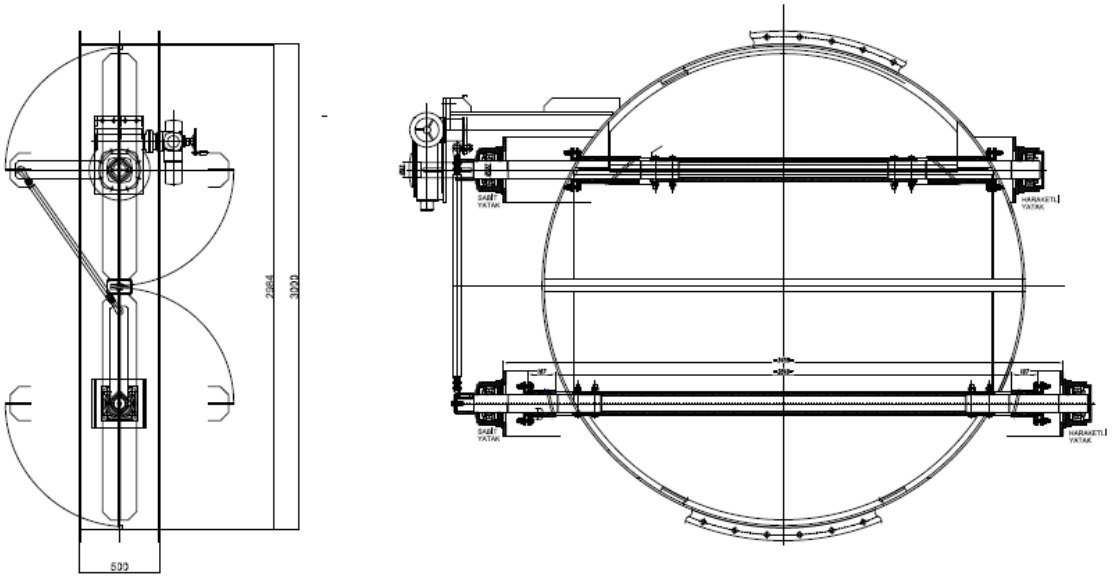
State of Art

The blades are currently made of AISI 310 type steel, since it has to resist in the hot environment inside the WHR (see KPI 9.5). Currently the blades are replaced every year, and they have an initial thickness of 8 mm8mm.

Test and Key Performance Indicators

Temperature resistance should be at least 450 °C,the coatings with high resistance to abrasion and thermal effects should be therefore used. The coating will be applied to a 300 × 100 flat plate, and it will be tested in the field. The success will be determined if the erosion appear to be 3 times less than the current steel used, corresponding to 3 years without replacing of the part. The comparison of the savings due to the reduced maintenance against the cost of the final FORGE coating will provide a direct evaluation of its possible uptake by the industry.

WHR Damper Blade



9.7 KPI 9.7: Wear resistance of raw mill fan blades

Criteria

In the Raw mill fan blade the blades are worn and repaired once in a year while the complete fan rotor is replaced in 5 year. Thus, ideally the target should be to make the fan blades last at least as long as the rotor (>5 years). Replacing some of the blades with coated ones will provide a direct evidence of the coating performace by measuring directly the coating thickness with ultrasonic thickness gauge. This might present some risk, in particular if the coating on the internal surface of the fan blades is not perfectly balanced, on the other hand to coat all the blades might not be feasible, therefore is expected that a partial coating on all the blades would solve the problem.

State of Art

The fan operates at 90 °C, raw meal dust and preheater outlet gas mixture environment. The blades are made ofST52-3 steel that when worn out and are repaired once in a year.

Test and Key Performance Indicators

The blades have dimensions of 970×365×150 mm and custom shape, will be coated with FORGE material from PT3 selection and tested in the process along with ST52-3 steel blades. The wear resistance of coated raw mill fan blades is expected to increase and to be measured after months of exposure by comparing with the uncoated blades. The comparison of the savings due to the reduced maintenance against the cost of the final FORGE coating will provide a direct evaluation of its possible uptake by the industry

Raw Mill Fan Blade

9.8 KPI 9.8: High temperature resistance of coated refractory bricks

Criteria

The resistance of coated refractory bricks is a key test that will define the performance and hence the suitability of the selected CCC coating developed under FORGE project. Refractory elements located in the industrial kilns used for firing ceramic tiles are exposed to harsh environments consisting of high temperature and combustion gases containing acid elements, mainly S, Cl and F, and metal vapours. Corrosion occurs on refractories surface after some time in service, leading to crack development and surface delamination.

Corrosion rate will be measured by relating the depth of deteriorated material (measured from the exposed to the harsh ambient) to the exposure time, and the units will be millimetres per year (mm/y).

The corrosion rate will be measured for both bare refractory brick and CCC-coated brick. A final corrosion rate lower than half of the value of the uncoated sample should be targeted. Hence, the ratio Corrosion rate (CCC-coated refractory brick)/Corrosion rate (refractory brick) is expected to be less than 0.5.

It should be taken into account that corrosion on refractories occurs after large exposure periods. It might be difficult to quantify a corrosion rate, especially if the exposure time within the framework of FORGE project is too short. So, time could be too short to develop measurable corrosion. To mitigate this risk, a qualitative comparison will be performed to evaluate, visually, the performance after service exposure.

State of Art

The refractory materials used in continuous roller kilns for firing ceramic tiles are mainly refractory bricks and other structural pieces used for building the dome. These materials will be the substrate where the CCC coating will be applied and tested.

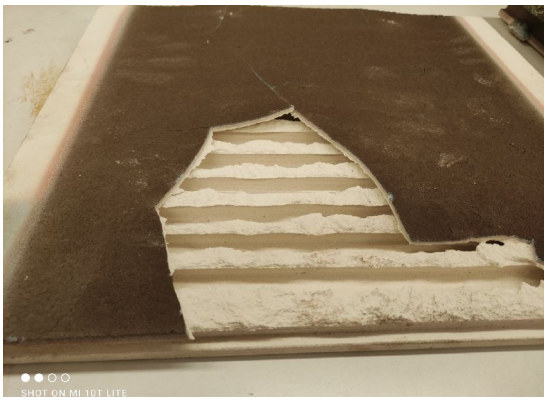
It has been observed that the expose surface of the refractories suffers from corrosion, due to the harsh conditions located in the kiln, which are mainly high temperature and combustion gases containing acid elements. The deteriorated layer is around 1 mm depth after being 6 years in service.

Test and Key Performance Indicators

The corrosion will be evaluated analysing the changes in the microstructure of the material. The samples will be mounted, in cross-section, in an epoxy resin and polished to a 1 µm finish using a diamond suspension. They will be then observed and photographed with the backscattered electron signal of a field-emission gun environmental scanning electron microscope (SEM). Thickness of the glassy layer formed on the surface of the refractories will be measured and characterized.

The CCC coating applied on the refractory elements of the kiln will be in service in the kiln during task 9.6. It will be tested under real industrial conditions, which involve high temperature (above 900 ºC), positive static pressure (0-2 Pa) and combustion gases containing acid elements and metal vapours (mainly alkaline which evaporate from the glaze applied to decorate the tiles).

Deteriorated piece of refractory, located at the dome of an industrial kiln



9.9 KPI 9.9: Profile geometrical accuracy after extrusion run

Criteria

Geometric tolerance measurement will be applied to the extrusion profiles which are attempted as the final products of the process made with extrusion dies improved by FORGE. Geometric tolerance measurement is needed to validate that the coating applied to the extrusion dies does not have any drawbacks on final products characteristics. As the final products of these dies are machined with CNC, extrusion profiles need to meet strict geometrical tolerances. This measurement will be applied using CMM (Coordinate Measuring Machine). The Profiles tolerances are determined as ±0.5 mm for open profiles top and bottom sections, ±1mm for open profiles right and left sections, +0.4 mm and -0.2 mm for solid profile top-bottom sections and ±0,3 mm for solid profile right-left sections.

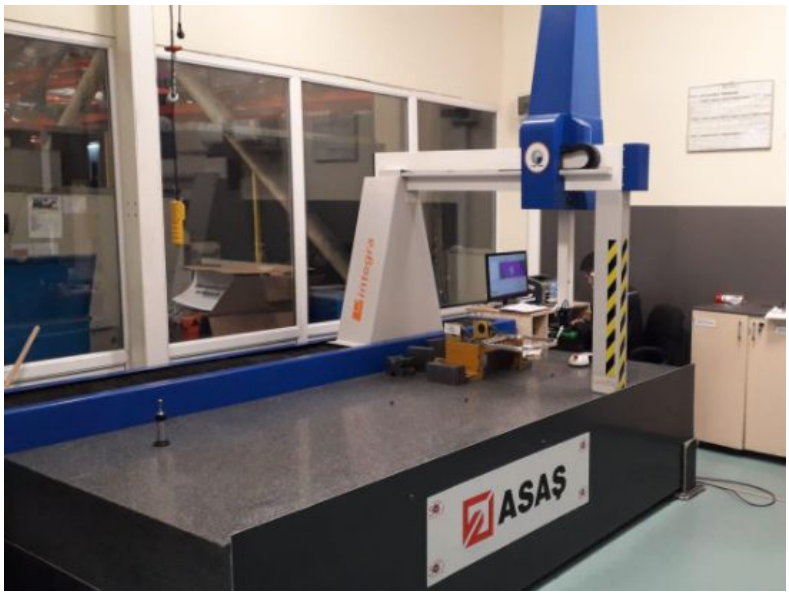
Only risk regarding this KPI can be attempted as possibility to access the component in time within the timeframe of the project. If this risk is faced than a control fixture or go - no go gage can be developed to speed up the process.

State of Art

Materials of extrusion profiles measured with CMM are high silicon content aluminium alloy for open profile die and high strength aluminium alloy for solid profile die. These same materials will be extruded using extrusion dies improved with FORGE coating.

Test and Key Performance Indicators

Tolerance measurement using CMM will be applied regarding to EN 755-3 and related customer requirements. Measurements carried out at room temperature. For open profile die products 300 mm of the profile and for solid profile die products 120 mm of the profile will be prepared as samples to measure profiles geometrical tolerances.



CMM (Coordinate Measuring Machine) used in ASAS for Geometric Tolerance Measurement

9.10 KPI 9.10: Profile recrystallised layer thickness after extrusion run

Criteria

Recrystallisation layer thickness measurement will be applied to the extrusion profiles which are attempted as the final products of the extrusion process. Recrystallised layer microstructures affect corrosion resistance of the extruded profiles, that is one if their key characteristic. If extruded with a die different from those currently used, the sliding wear might change the local maximum temperature reached by the extruded profile and consequently the recrystallisation layer that is formed during the profile cooling. This measurement will be applied using Optical Microscope. Recrystallised layer thickness should be below 200 µm.

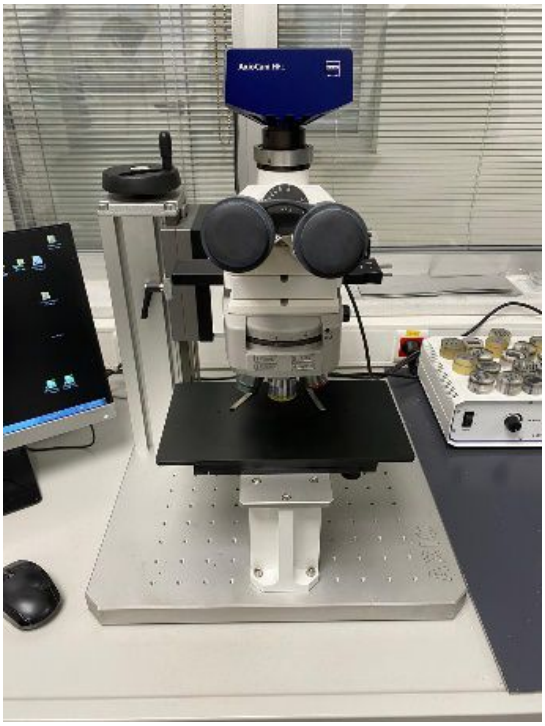
Only risk regarding this KPI can be attempted as possibility to access the component in time within the timeframe of the project since sample preparation takes too much time and precise. If this risk is faced than sample numbers can be reduced according to initial results and process parameters.

State of Art

Materials of extrusion profiles which are subjects of metallographic analysis are high silicon content aluminium alloy for open profile die and high strength aluminium alloy for solid profile die. These same materials will be extruded using extrusion dies improved with FORGE coating, and the recrystallization layer benchmarked.

Test and Key Performance Indicators

Metallographic analysis using optical microscope will be applied to the extrusion profiles with respect to general metallographic investigation route. Measurements carried out at room temperature. Sample preparation includes cutting, mounting to bakalite, grinding and polishing. Sample dimension for this analysis is 40×40×20 mm.



Metallographic Microscope for the measurement of the Recrystallization layer

9.11 KPI 9.11: Profile tensile strength and elongation after extrusion run

Criteria

Tensile strength and elongation measurement will be applied to the extrusion profiles which are attempted as the final products of the extrusion process. It will be measured using tensile testing equipment, in order to check final products quality after FORGE solution application to the extrusion dies. Measured values must be within the limits to validate that the coating applied to the extrusion dies does not have any drawbacks on final products characteristics. Profiles extruded by open profile die should have minimum 480 MPa yield strength, minimum 540 MPa tensile strength and minimum 5 % elongation value. Profiles extruded by solid profile die should have minimum yield strength between 260-480 MPa, minimum 310 MPa tensile strength and minimum 7 % elongation value. According to these values it will be evaluated that mechanical property difference may be caused from FORGE solution.

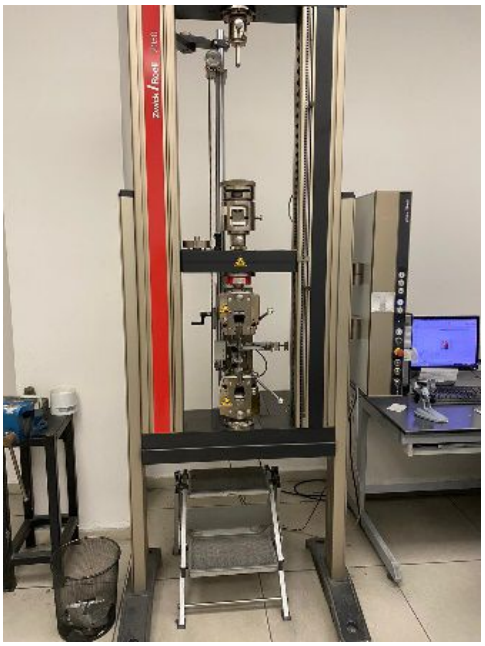
The only and minor risk can be time restrictions. If it may not be possible to measure determined number of profiles, sample numbers can be reduced regarding process parameters and initial results of the trials.

State of Art

Materials of extrusion profiles measured with Tensile Test are high silicon content aluminium alloy for open profile die and high strength aluminium alloy for solid profile die. Average values of open profiles are 500 MPa yield strength, 550 MPa Tensile strength and 10% elongation. Average values for solid profiles are 300 MPa yield strength, 350 MPa tensile strength and 8% elongation.

Test and Key Performance Indicators

Profile tensile strength and elongation after extrusion run will be measured via the Tensile testing equipment with respect to ISO 6892-1. For open profile die products 300 mm of the profile and for solid profile die products 120 mm of the profile will be prepared as pre-samples for tensile test.



9.12 KPI 9.12: Profile hardness after extrusion run

Criteria

Hardness measurement will be applied to the extrusion profiles which are attempted as the final products of the extrusion process. Hardness will be evaluated via Brinell Hardness (HB), in order to check final products quality after FORGE solution application to the extrusion dies. Measured values must be within the limits to validate that the coating applied to the extrusion dies does not have any drawbacks on final products characteristics. Profiles extruded by open profile die must be between 140 and 170 HB. Profiles extruded by solid profile die must be between 92 and 112 HB.

The only and minor risk can be time restrictions. If it may not be possible to measure determined number of profiles, sample numbers can be reduced regarding process parameters and initial results of the trials.

State of Art

Materials of extrusion profiles measured with Brinell Hardness are high silicon content aluminium alloy for open profile die and high strength aluminium alloy for solid profile die. Average Brinell Hardness value for open profile die products 155 HB and for solid profile die products 101 HB.

Test and Key Performance Indicators

Hardness will be evaluated via the Brinell hardness test with respect to AMS2658D and ASTM E10. For open profile die products 300 mm of the profile and for solid profile die products 120 mm of the profile will be prepared as a Brinell Hardness Sample.

Hardness Tester

9.13 KPI 9.13: Weight of billets per die

Criteria

Performance measurement of FORGE Solution will be done by calculating the total weight of billets extruded before the appearance of failures in the extrusion die. This KPI will demonstrate if coating developed within this project increased extrusion dies wear resistance or not. It is expected to extrude more than 2 tons of billets, that is the current average extrusion die performance.

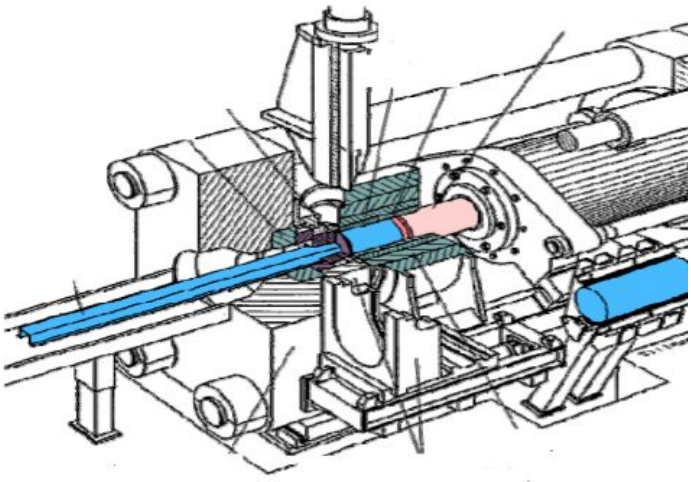
Since the appearance of cracks and scratches, that are indicative of a coating failure in the die, are determined by visual inspection, some kind of flaws appearing in the inner parts of the profile, and not directly visible by the operator, can result in undetermined initial failure time. To prevent this risk to happen, length cutting operation can be applied after the extrusion of each billets. If it cannot be controlled with the cautions, trial must be repeated.

State of Art

Current extrusion dies are made in 1.2344 (AISI H13) steel for open profile die, and 1.2367 (X38CrMoV5-3) for solid profile, all the dies are then nitride to enhance the steel resistance to slide wear. SoA value of billets weight extruded is 2 tons. Extrusion dies are replaced with backup dies after 2 tons of aluminium billets extrusion.

Test and Key Performance Indicators

Extruded billets weight measurement will be applied by multiplying one billets weight with number of billets extruded. Extrusion conditions are, 280 bar and 480°C peak temperature for solid profile and 300 bar and 490°C peak temperature for open profile.



The greenish part indicated the position of the extrusion die

10 TABLE OF KPI (OVERVIEW)

Chapter 10 is comprised of Table 1 which delivers an overview of KPIs of Work Packages 2 - 9 of the FORGE project.

Table 1:Table of Key Performance Indicators for WP2, WP3, WP4, WP5, WP6, WP7, WP8 and WP9 of the FORGE project.

KPI number	KPI Name	Performance target	Test name (standard)	Quantity measured directly from test	KPI	KPI target value	KPI Units
WP2							
2.1	Hardness	PT3	Vickers hardness (ASTM E92)	Hardness (HV10)	Deviation from ML predicted hardness	<10	%
2.2	H_2 charging	PT2	charging via a solution containing (hydrogen or deuterium) + Thermal Desorption Spectra (TDS) (diffusible hydrogen)	H_2 content after charging (ppm)	H_2 content after charging (ppm)	<SoA value	ppm
2.3	HNO_3 resistance (cast specimens)	PT1	Linear Polarisation Resistance (ASTM G59/G102)	Corrosion rate (mm/y)	Corrosion rate	<0.1	mm/y
2.4	Nanohardness	PT3	Nanohardness (ISO 14577)	Hardness (HV)	Deviation from ML predicted hardness	<10	%
2.5	H_2 charging	PT2	Hydrogen charging followed by nanoindentation (customised test)	Hardness (HV)	Hardness variation	<10	%
2.6	HNO_3 resistance (PVD patterns)	PT1	Droplet corrosion (customised test)	Corrosion rate (mm/y)	Corrosion rate (thickness loss)	<1	mm/y
2.7	Cost	PT1, PT2, PT3	n/a	Cost (€/kg)	Cost	<30	Cost (€/kg)

KPI number	KPI Name	Performance target	Test name (standard)	Quantity measured directly from test	KPI	KPI target value	KPI Units
WP3							
3.1	Porosity (sol route)	PT4	Archimedes mehod (DIN EN 623-2)	Porosity (vol%)	Porosity	<5	vol. %
3.2	Corrosion rate	PT4	Microstructural analysis after corrosion exposure (customised)	Corrosion rate (mm/y) from (mm/run)	Corrosion rate (CCC-coated refractory brick)/Corrosion rate (refractory brick)	<0.5	[-]
3.3	CTE (sol route)	PT4	Dilatometry (DIN EN 821)	CTE (10^{-6}/K)	Deviation from brick CTE	<200 CTE (coating)-CTE (brick) < +-2 ppm	%
3.4	Porosity (powder route)	PT4	Archimedes method (DIN EN 623-2)	Porosity (vol%)	Porosity	<5	vol. %
3.5	Corrosion rate	PT4	Microstructural analysis after corrosion exposure (customised)	Corrosion rate (mm/y)	Corrosion rate (CCC-coated refractory brick)/Corrosion rate (refractory brick)	<200	[-]
3.6	CTE (powder route)	PT4	Dilatometry (DIN EN 821)	CTE (10^{-6}/K)	Deviation from ML-predicted CTE	<200 CTE (coating)-CTE (brick) < +-2 ppm	%
3.7	Cost	PT4	n/a	Cost (€/kg)	Cost	≤60	Cost (€/kg)
WP4							
4.1	PT1 Mean Machine Learning Root Mean Square Error (RMSE)	PT1	n/a	RMSE (**mm/y**)	RMSE	<0.1	mm/y
4.2	PT2 Mean Machine Learning Root Mean Square Error (RMSE)	PT2	n/a	RMSE (**hardness variation HV**)	RMSE	<10	HV
4.3	PT3 Mean Machine Learning Root Mean Square Error (RMSE)	PT3	n/a	RMSE (**HV**)	RMSE	<50	HV
4.4	PT4 Mean Machine Learning Root Mean Square Error (RMSE)	PT3	n/a	RMSE (**CTE**)	RMSE	<1	(10^{-6}/K)

KPI number	KPI Name	Performance target	Test name (standard)	Quantity measured directly from test	KPI	KPI target value	KPI Units
WP5							
5.1	Powder Hall flowability	PT1, PT2, PT3	**ASTM B213** – 03 Method for Flow Rate **ASTM B923 – 02** Method for Metal Powder Skeletal Density	Flowability (s/CC)	Flowability, the time it takes to 50g of powder to pass through a standardized orefice	<5	s/CC
5.2	Powder flowability - Hausner Ratio	PT1, PT2, PT3	**ASTM B527-93** r Determination of Tap Density **ASTM B212 – 99** Apparent Density	Hausner ratio (-)	Hausner ratio: The Tap density value devided by the bulk (apparent) density value	<1,3	[-]
WP6							
6.1	Porosity (CCA)	PT1, PT2, PT3, PT4	Metallographic examination	Porosity (area %)	Porosity	< 5	area %
6.2	Coating cracks	PT1, PT2, PT3, PT4	Metallographic examination	Number of cracks	Number of cracks	None	[-]
6.3	Coating/substrate interfacial delamination	PT1, PT2, PT3, PT4	Metallographic examination	Interfacial delamination	Interfacial delamination	None	[-]
6.4	Erosion wear	PT3	Erosion wear test (ASTM G76)	Wear rate (g/min)	Wear rate	<0.071	g/min
6.5	Porosity (CCC)	PT4	Archimedes method (DIN EN 623-2)	Porosity (vol%)	Porosity	<5	vol. %
6.6	Corrosion rate	PT4	Microstructural analysis after corrosion exposure (customised)	Corrosion rate (mm/y)	Corrosion rate (CCC-coated refractory brick)/Corrosion rate (refractory brick)	<200	[-]
6.7	CTE	PT4	Dilatometry (DIN EN 821)	CTE (10^{-6}/K)	Deviation from ML-predicted CTE	<200 CTE (coating)-CTE (brick) < +-2 ppm	%

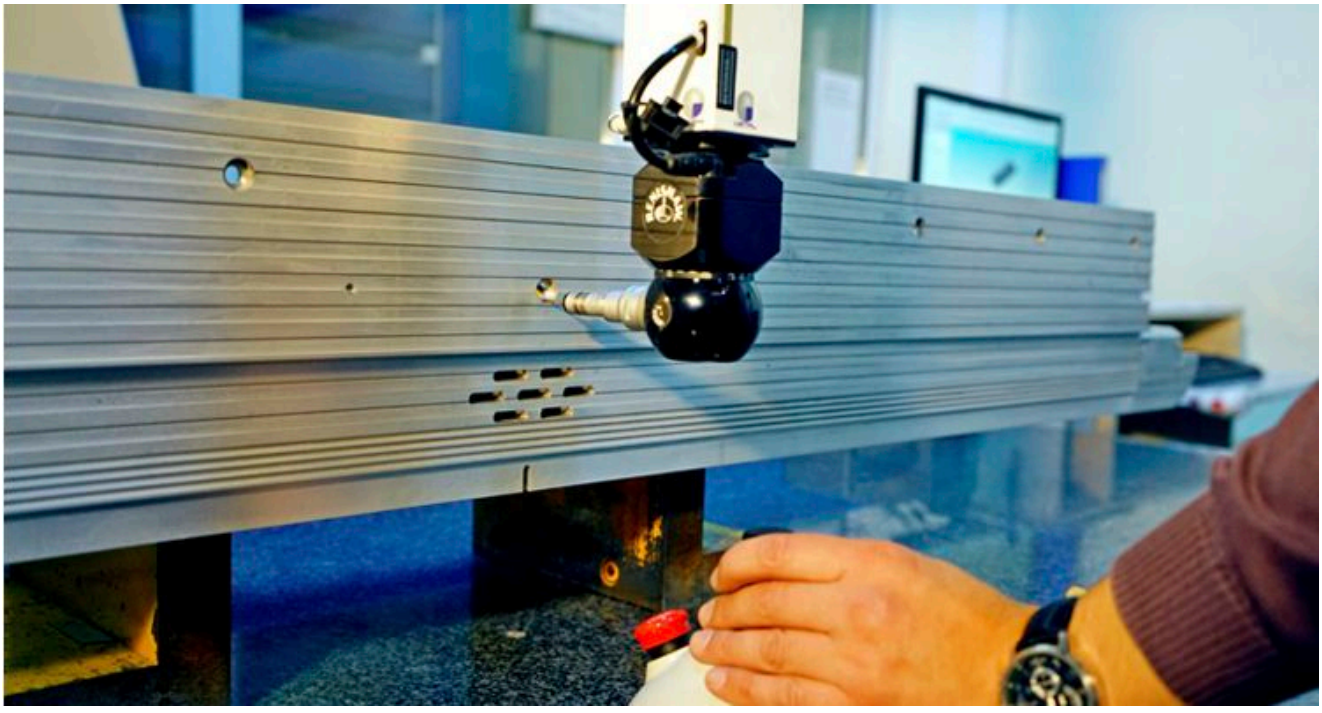
KPI number	KPI Name	Performance target	Test name (standard)	Quantity measured directly from test	KPI	KPI target value	KPI Units
WP7							
7.1	HNO_3 resistance (Coatings)	PT1	Exposure test (ASTM G1/G157/G31)	Corrosion rate (mm/y)	Corrosion rate (thickness of corrosion affected area measured via metallographic examination)	<1	mm/y
7.2	H_2 pick-up	PT2	gaseous charging + hot extraction	H2 content after charging (wtppm)	H2 content after charging (wtppm)	SoA value	ppm
7.3	Resistance to abrasive wear	PT3	Abrasive wear test (ASTM G65)	Volume loss (mm^3)	Volume loss	<80 (+/-10)*	mm^3
7.4	Cracking after high temperature and thermal cycling	PT4	Microscopic examination	Number of cracks/mm of interface	Cracking	None	[-]
7.5	Interfacial delamination after high temperature and thermal cycling	PT4	Microscopic examination	Interfacial delamination/mm of interface	Interfacial delamination	None	[-]
7.6	Corrosion after high temperature and thermal cycling	PT4	Microscopic examination	Corrosion rate (mm/y)	Deviation from brick corrosion rate	<50	%
7.7	Sliding wear	PT3	Pin on Disk (ASTM G99)	Wear rate (mm/y)	Wear rate (CCA)/Wear rate(SoA)	<0.8	[-]
WP8							
Taggants							
8.1	Emission intensity	PT3	Spectral emission intensity	Number of photons at maximum emission wavelenght	Ratio: Number of photons emitted at max (excitated with maximum excitation wavelength) / number of photons emitted of reference material (010-000013 at 626 nm (excitated at 365 nm)	> 20%	%

KPI number	KPI Name	Performance target	Test name (standard)	Quantity measured directly from test	KPI	KPI target value	KPI Units
8.2	Emission quenching temperatures	PT3	Spectral emission intensity as function of temperature	N° of photons at maximum emission as function of temperature	TQ50 - Quenching temperature TQ95 - Total Quenching Temperture	TQ50>350; TQ95>550	K
8.3	Optical emission at extreme conditions [after exposure to oxygen at high temperature (static and cyclic) exposure to forming gas]	PT3	Spectral emission intensity as function of O2 or forming gas at high temperatures (static and cyclic)	N° of photons at maximum emission after temperature treatment in oxygen or forming gas flow	Ratio: number of photons emitted at a maximum for post-treated sample/number of photons emitted at a maximum for samples measured at standard conditions	> 70% just thermal treatment >20% under gas flow	%
Coatings and Sensor							
8.4	Sensor performance in WHR environment	PT3	Custom test	Spectral form and intensity of selected taggant	Presence of spectral features (peaks, bands) of adequate intensity of selected taggant prior and post exposure of the sensor	Spectral Features at ±5nm Intensity > 10% with regards to the room temperature analysis	[-]
8.5	Adhesion strength	PT3	Pull-off adhesion strength (ASTM C633 or D4541)	Adhesion strength (MPa)	Adhesion strength (CCA+taggant)/Adhesion strength (CCA-only)	≥ 80%	[-]
WP9							
9.1	Resistance to corrosion in CO_2 rich environment	PT1	Linear Polarisation Resistance (ASTM G59/G102)	Corrosion rate (mm/y)	Corrosion rate	<1	mm/y
9.2	Resistance to H_2 pressure (disk rupture)	PT2	Disk rupture test (ISO 11114-4)	H_2 rupture pressure ratio (-)	H_2 rupture pressure ratio	1.5<x<2	P_{He}/P_{H2}
9.3	Resistance to H_2 pressure (permeation)	PT2	High pressure Permeation test	Diffusion coefficient (cm^2/s)	Diffusion coefficient	$<3\cdot10^{-11}$	cm^2/s
9.4	Resistance to impact wear	PT3	Impeller tumbler test	Wear rate (mm/y)	Wear rate specimen/Wear rate (SoA)	>1.2	[-]

KPI number	KPI Name	Performance target	Test name (standard)	Quantity measured directly from test	KPI	KPI target value	KPI Units
9.5	Wear resistance in Waste Heat Recovery (WHR) system circular duct	PT3, PT4	Coating thickness monitoring after service exposure	Coating thickness (mm)	Time to replacement	>9	years
9.6	Wear resistance in Waste Heat Recovery (WHR) system damper blades	PT3, PT4	Coating thickness monitoring after service exposure	Coating thickness (mm)	Time to replacement	>3	years
9.7	Wear resistance of raw mill fan blades	PT3, PT4	Coating thickness monitoring after service exposure	Coating thickness (mm)	Time to replacement	>5	years
9.8	High temperature resistance of coated refractory bricks	PT4	Microstructural analysis after corrosion exposure (customised)	Corrosion rate (mm/y)	Corrosion rate (CCC-coated refractory brick)/Corrosion rate (refractory brick)	<0.5	[-]
9.90	Profile geometrical accuracy after extrusion run	PT3, PT4	Profile geometrical tolerances (EN 755-3)	Geometric tolerance (mm)	Geometric tolerance	Open profile top-bottom: ±0,5 Open profile right-left: ±1 Solid profile top-bottom: +0,4, -0,2 Solid profile right-left: ±0,3	mm
9.10	Profile recrystallised layer thickness after extrusion run	PT3, PT4	Metallographic analysis	Recrystalised layer thickness (µm)	Recrystalised layer thickness	<200	µm
9.11	Profile tensile strength and elongation after extrusion run	PT3, PT4	Profiles Tensile Test (ISO 6892-1)	Tensile strength and elongation (MPa, %)	Tensile strength and elongation	Open Profile: min. 480 (YS), min. 540 (TS), min. 5% elongation Solid profile: 260-480 (YS), 310 (TS), min. 7%	MPa, %
9.12	Profile hardness after extrusion run	PT3, PT4	Profile Hardnes Test (AMS2658D), (ASTM E10)	Brinell Hardness (HB)	Brinell Hardness	Open profile: 140<value<170 Solid Profile: 92<value<112	HB
9.13	Weight of billets per die	PT3, PT4	Metallographic analysis	Weight of billets extruded (tons)	Weight of billets extruded (tons)	>2	[tons]

11 CONCLUSIONS

This report has provided an overview of the project KPIs in the FORGE project. This has been presented in a table format as well as a thorough analysis of the criteria, state of art and testing methodologies of each KPI. The KPIs classified in this report will be used to guide the technical activities in the project and to initially set the parameters that will help to determine the success of the novel coating materials. As the FORGE project continues to progress, the KPIs will be monitored and updated during the project as more stages are completed targeting the development and optimisation of components used in energy intensive industries.



Quality measurements in ASAS