THE FUTURE COATING FOR OFFSHORE RIGS AND SHIPS

NEW CERAMIC COATINGS ON METALIC SURFACES
INTRODUCTION

These advanced coatings are aimed to protect metallic surfaces (mainly steels and alloys) in very aggressive environments.

They are originated by a controlled melting process of different INORGANIC materials mainly Quartz which is the responsible of most of their resistant properties

The COATING process consists on :

1- Metallic surface conditioning: normally by sand blasting
2- Raw Ceramic coating application in several available ways (wet or dry. From wet gun spraying to Thermal sparying … etc ..)
3. Vitrification of the coating in a range from 700ºC to 900ºC Tratamiento térmico en el rango de 700 a 900ºC during short times (from seconds to 10 min) depending on substrate and ceramic combination

These processes obtain a very smooth and vitreous surface ,very hard, with a chemical adherence to the metal and with the same expansion coefficient

Its most remarkable properties are :

Non permeable surface
Aseptic (Inhibits bacterial growth)
Hygienic (Easy-to-clean)
High temperature resistance (up to 850ºC metal temperature)
High chemical corrosion resistance
Sun Light resistance (colour stability)
Environmental corrosion resistance
High hardness (scratch and abrasion)-64 HrC
Environmentally Friendly (100% recyclable – an not LEACHING any element

Other secondary properties:

Lubricity - low friction applications
Adhesion - resistance to damage by impact, torsion, bending (1'2% elongation) or thermal shock (From 650ºC to 0ºC in seconds in water
Relative Impact resistance - not fracture due to impact below 1'2% elongation on substrate

Flexibility - good flexibility and adhesion when applied to thin metal substrates
Stiffening - because of its low ductility and intimate bond
Thickness - wide range of thickness 50 to 300 microns normally)
Resistance to thermal oxidation/corrosion - provide both protection of the metal and ease of cleaning.
Thermal stability - ability to withstand intermittent or prolonged heat
Thermal expansion – designed to be the same as the substrate.
Emissivity – **Absorptivity** power of a surface to release heat by radiation
Thermal conductivity range ≈ 5-8 w/mk // average (reference) ≈ 6w/mk.
Dielectric strength - normal is 200 to 500 volts/mil
Volume resistivity dielectric constant - at 400-cycles per second and at room temperature, the dielectric constant is in the range of 6 to 12.
Dissipation factor - at 400-cycles per second and room temperature, the dissipation factor is about 1 or 2 %.

These coatings are ALREADY BEING APPLIED MAINLY IN TUBULAR ARRANGEMENTS as most of tubes can be vitrified in gas or electric (resistance & or induction furnaces)

Tubular Application links : https://www.tubacoat.com/ pay attention to the practical downloads

Tubes and parts with this conventional process HAVE BEEN SUCCESSFULLY TESTED IN SEA WATER DURING YEARS .. WITHOUT ANY DAMMAGE …..BUT

BUT large steel structures as offshore wind towers, monopiles, TP's or mainly SHIP HULLS **can not be vitrified in any furnace**…not only by size and amount of energy required, but for the damage to the steek at these temperatures

THAT'S WHY we are developing a new vitrification (and application) fully automated process on robots capable of:

- **Apply the coating over a conventionally sand blasted surface**
- **Vitrify it to the adequate superficial temperature by Laser VCSL technology**
- **Perform the holyday test quality control inn real time**

ALL incorporated in the same Robot head … if possible
The targeted process speed is to coat 1m ^{2} / min …if possible

PROJECT SITUATION AS PER JAN 2024

- Ceramics have been developed to maintain same properties (or better) than furnace vitrification but adapted to :
- Robot application including drying
- High absorptivity (0ver 98%) in order to maximize the laser energy

During most of 2023 samples have been tested by TECNALIA on his HARSHLAB on the Sea and in. accelerated tests in lab

And here we present and explain the successful results which encourage us even more to fulfill this endeavor

CERAMIC COATING REAL SEA TEST in TECNALIA'S HARSHLAB RIG

SAMPLES TESTED:

- FURNACE VITRIFICATION: Conventional : Not suitable for big parts
- LASER VITRIFICATION : New development to vitrify big parts by robots

TESTS PERFORMED:

- At lab : **Cyclic test as per ISO 12944-9:2018**
- At sea in the HARSH LAB RIG during 6570 Hrs
    - Submerged
    - Splash zone

DESCRIPTION OF SAMPLES TESTED

- FURNACE VITRIFICATION : Today's industrial standard

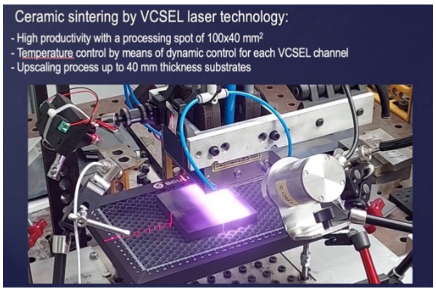
Substrate steeel: S355J2 8mm Thick
Surface conditioning – Sandblasted with white corundum
Ceramic 1 – Water suspension
Aplication – Hand air gun spray
Driying –Stove at 80ºC
Vitrification –Electrical furnace 780ºC 6'

Sample:

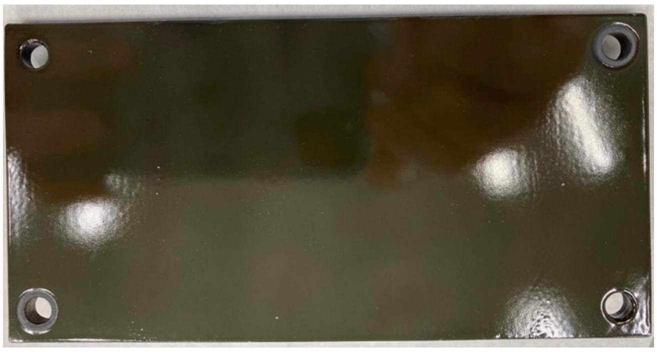
- LASER VITRIFICATION with VCSEL

Sustrate Steel S355J2 8mm thick
Surface conditioning – Sandblasted with white corundum

Ceramic 2 – Dry powder applied by Thermal Spray
Vitrification – VCSEL



SAMPLE :



PREVIUOS DATA TO FULLY UNDERSTAND THE TEST EVALUATION PROCEDURES

CERAMIC STRUCTURE AND CHEMICAL BONDING MECHANISM

Chemical composition of enamel, the type of steel, the gases that might be solved in the steel, the roughness of the metal surface, the heating process ,the temperature of vitrification and the atmosphere of heating environment are the factors affecting the interface reactions and so adhesion mechanism between ceramic glassy coating and metal substrate.

The Chemical Bonding between the metal surface and the ceramic coating is the result of complex reactions at the metal/enamel phase boundary.

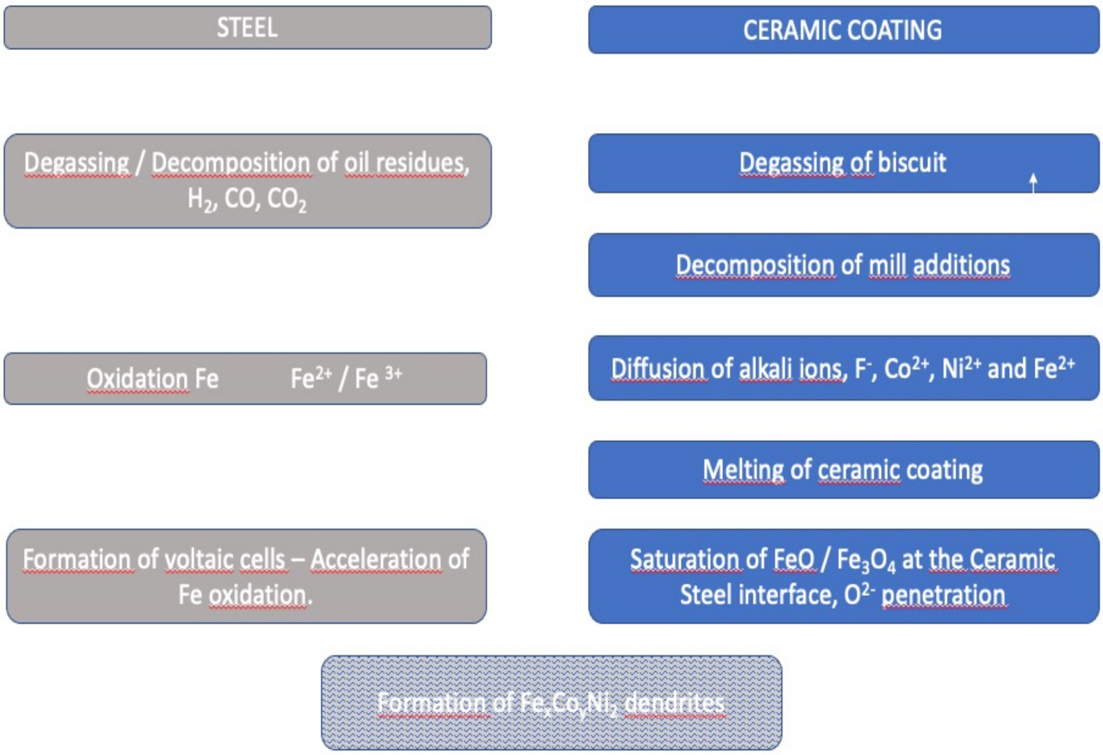


Figure 1: Reactions during vitrufication of Ceramic Coating on Steel

STEEL AND CERAMIC COATING REACTIONS DURING VITRIFICATION

BUBBLE STRUCTURE FORMATION

“Bubble Structure” is a characteristic of some coatings and depends strongly on the heating conditions.

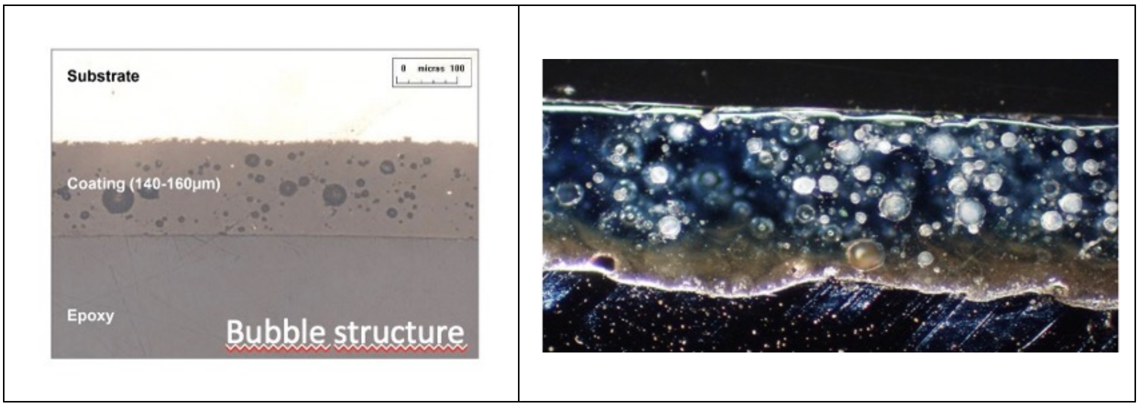


Figure 2: Bubble Structure

Coatings completely free of bubbles have a lower elasticity and hence are more sensitive to impact and tend to chip off.

Related reactions:

1- IN THE CERAMIC COATING

Degassing of residual H_2O in powder enamel and decomposition of application additives

At about 500ºC, there is an additional water vapor formation. This vapor remains in the ceramic coating, partly in form of fine bubbles.

2- IN THE STEEL – during the heating ramp there is a certain degassing; H_2, CO, CO_2 that might get sequestered in the ceramic
95% of the research made in different institutions about the composition of these bubbles conclude that is practically only H_2 the fraction that gets clogged on the ceramic layer

3- INTERFACE DIFFUSION LAYER

In this phase, the most important processes are creation of the metal-enamel boundary formed by diffusion of Fe from steel surface to the glass. This causes the formation of a layer of iron oxide at the enamel/steel interface.

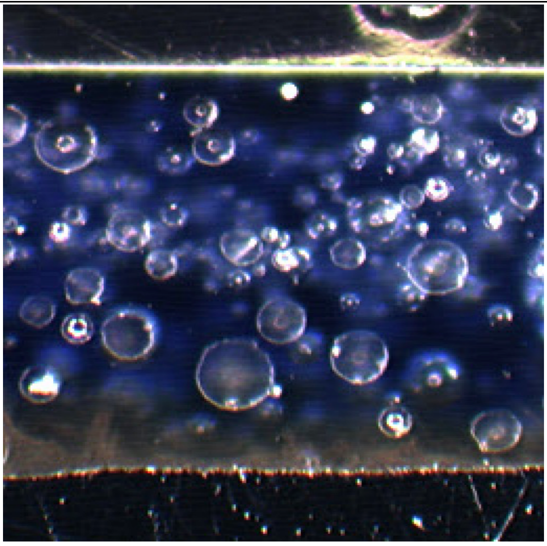
	**EPOXI** **CERAMIC COATING BUBBLE STRUCTURE** **INTERFACE DIFFUSION LAYER** **STEEL**

Figure 3

Related reactions:

STEEL - Oxidation of Fe to Fe^{2+} + Fe^{3+}

The metal surface oxidizes. The O_2 present in the air penetrate the porous enamel before or during vitrification and oxidize the Fe in the steel. It is only thin oxide layer that causes the surface to be wetted by the melting ceramic coating at temperature above 600ºC.

STEEL AND CERAMIC COATING - Iron dissolution.

Ceramic coating softens and melts forming a semi-permeable layer.
This reduces gaseous exchanges with the furnace atmosphere.
The Iron oxide just being formed dissolves in the molten enamel. D
ue to the
concentration gradient, it diffuses into the enamel layer.

CHEMICAL BONDING

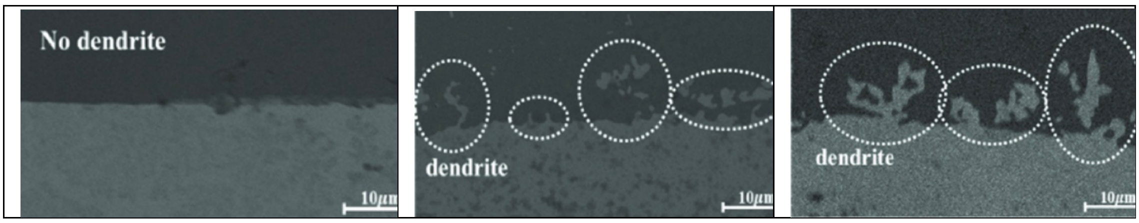
Figure4; Impact test results showing – good adhesion - Poor adhesion

The third stage is around 830 deg C. At this temperature chemical redox reactions take place between the iron oxide layer at the enamel/steel interface. Fe-Co-Ni alloys precipitate at the enamel/steel interface. These are at the heart of the adhesion of enamel to steel.

Related reactions:

STEEL AND CERAMIC COATING - Formation of $Fe_xCo_yNi_2$ dendrites.

Iron oxide penetrates into the coating layer and at same time Cobalt and Nickel ions are reduced at the phase boundary to dendritic crystals of metallic Cobalt or Nickel and their alloys with iron. This f**orms**, along with the iron, local voltaic cells, which promote (accelerates) the oxidation of the base metal. The iron surface thus becomes very rough and produce many anchor points for the ceramic coating.



Figure; dendritic structure

Due to these reactions, there are NOT two separated layers as in most of the coatings so exfoliation or full cracking never reaches the steel underneath

The amorphous structure of the ceramic is also a very good defense against cracking as there are NO grains so that might only happen due to impacts with a deformation above 1’2% so relatively strong (plastically deforming the steel below)

HARSHLAB – MICROSCOPIC EVALUATION

Once the plates passed the 9 months sea tests we made the following microscopical inspection

Procedure:

Preparation . small pieces are cut and embedded in resin to be transversally observed

One of the pieces was taken from the splash area and the other from the submerged one

Both being laser vitrified

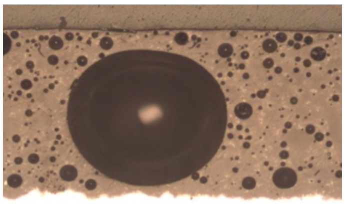
Points of interest:

1. **Diffusion area** or Red-Ox reactions zone : It must be of a thickness of about 10% of the total coating thickness

   A thinner diffusion area implies a lower adherence
   A thicker area indicates overheating that might damage the bubble structure and the ceramic itself

2. **Average coating thickness :** a good average for obtaining a strong coating layer is between 150 and 250 microns
   As the tested plates were **hand made,** some points have thickness out of that range

3. **Bubble structure :**
   A Good structure must have bubbles with diameters not exceeding the 20% of the total thickness and NO big bubbles as for instance the one in the picture below



Result:

Please amplify & turn for better scrutiny

2023089 KERACOAT HARSHLAB MICROSCOPIC ANALYSIS

Target is to inspect the bubble structure after 9 months at sea in the Harshlab rig inmersion & splash zones.
Two plates , 1L & 5L LASER vitrified are inspected
Marks indicate the cut areas from where the probes were taken

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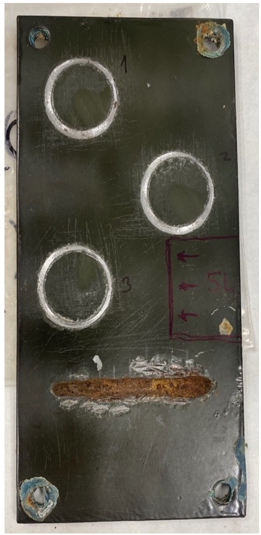
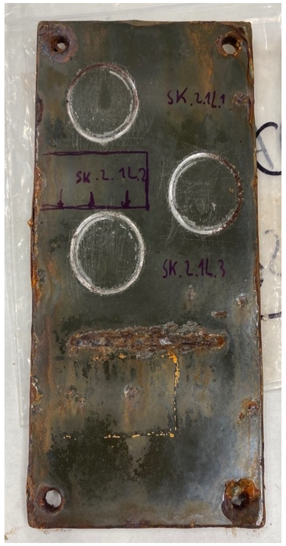


PLATE 1L



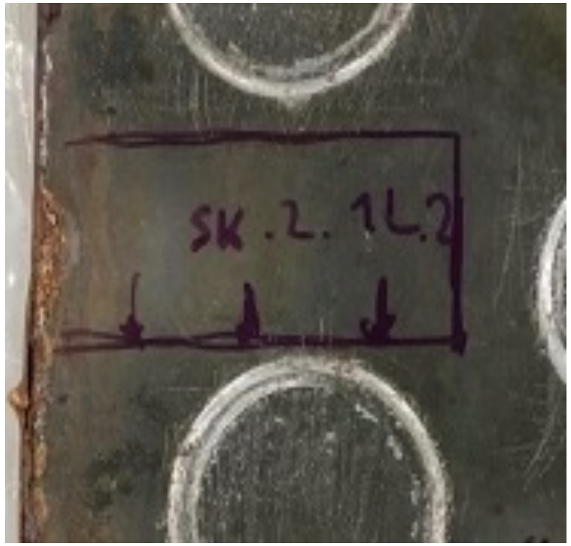
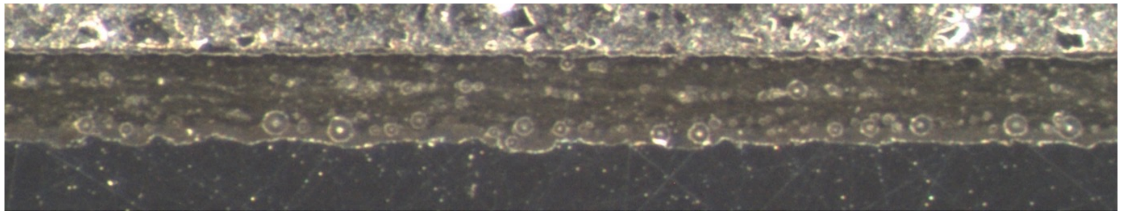


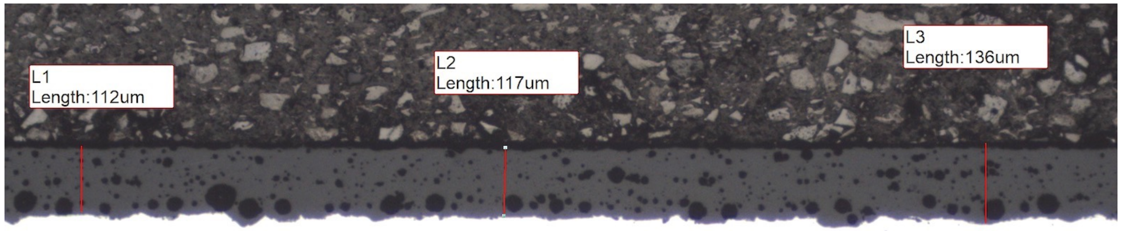
PLATE 5L

MICROSCOPIC ANALYSIS

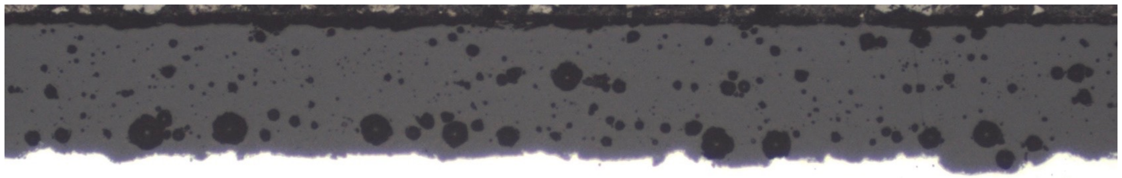
PLATE 1L

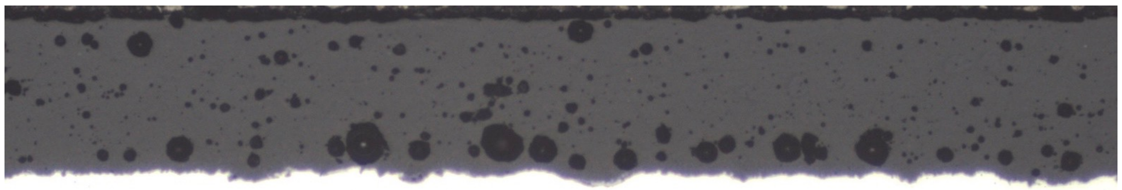


DIFFUSION AREA : a bit in the BIG side
but around standard



Average thickness :
122 microns, a bit low …. Hand made

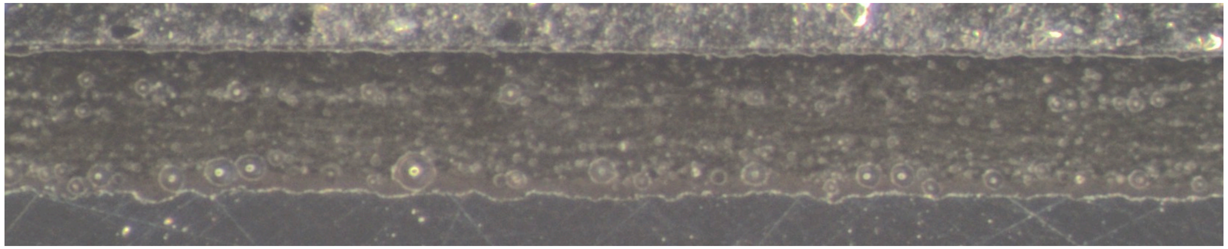




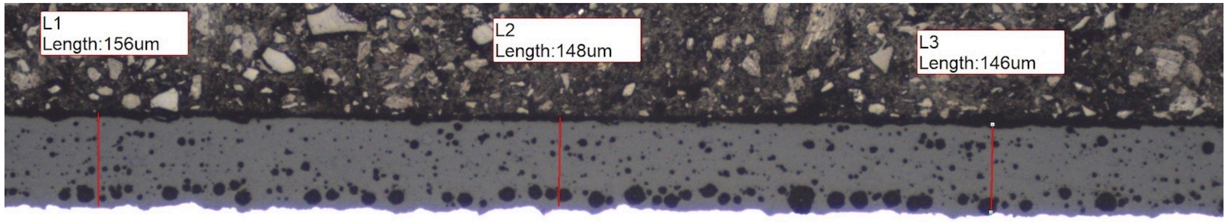
Bubble structure:GOOD Goods ize
average and no big ones close to
Surface

2023089 KERACOAT HARSHLAB MICROSCOPIC ANALYSIS

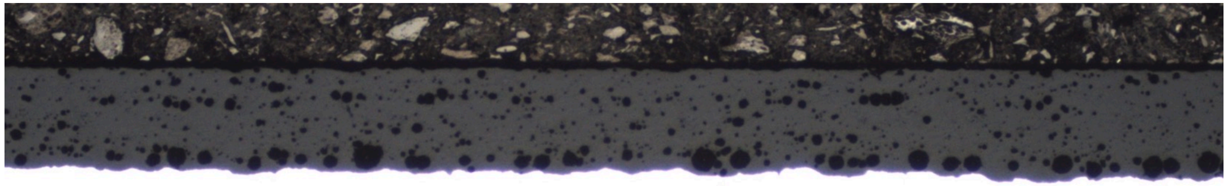
PLACA 5L

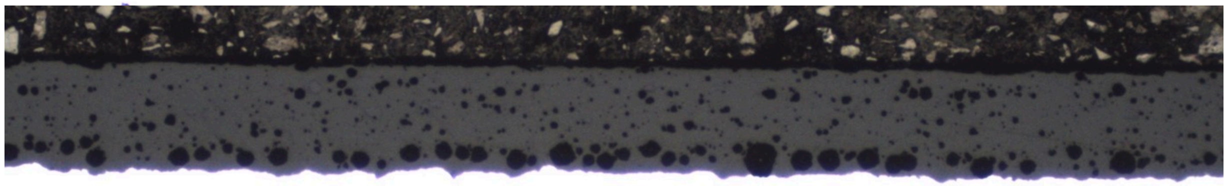


DIFFUSION AREA : a bit in the BIG side but around standard



Average thickness :
150 microns





Bubble structure: very Good .

Average size, medium- small and closer to the Steel .

CONCLUSION

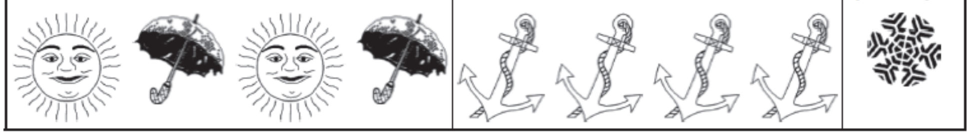
In both plates (splash and submerged) the bubble structure is quite good with adequate size and quantity as to guarantee sufficient adherence and elasticity and without any risk of big bubbles close to the surface.

The Surface is smooth, continuous and with not a single point of damage or lost of material after the tests and water jet cleaning operation.

LABORATORY - CYCLIC TEST AS PER ISO 12944-9:2018

Procedure: plates are subject to an accelerated aeging propcess during 168 hrs according to the following tests

Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
UV/condensation — ISO 16474-3			Neutral salt spray — ISO 9227			Low-temp. exposure at (−20 ± 2) °C



a) 72 hrs under UV light and condensation as per **Norm ISO16474-3**(2)
b) 72 hrs in salty chamber as per **Norm ISO9227**(3)
c) 24 hrs at low temperature(-20°C ± 2°C)

total test time **4200h (25 cicles)**

Short explanation of procedures :

(1) ISO 12944-9:2018 - Corrosion protection of steel structures by protective paint systems. Part 9: Protective paint systems and laboratory performance test methods for offshore and related structures.
(2) ISO16474-3 - Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps.
(3) Norma ISO9227 - Corrosion tests in artificial atmospheres - Salt spray tests.

ENTALLA: SCAR or *scribe* made by artificial means

Results:

LABORATORY - CYCLIC TEST AS PER ISO 12944-9:2018

Results:

PLATE 9L LASER–VCSEL		
PLATE 3 Furnace vitrification		

a) The only oxidation observes was in the sharp edges and in the scar, as there in no coating there : NO OXIDATION ON THE SURFACE

b) Adherence as per UNE-EN-ISO 4624:2016 VERY GOOD , see the particular test explanation of the Pull-off test

d) There are not differences due to the diverse vitrification processes.

(1) ISO 12944-9:2018 - Corrosion protection of steel structures by protective paint systems. Part 9: Protective paint systems and laboratory performance test methods for offshore and related structures.
(2) ISO16474-3 - Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps.
(3) Norm ISO9227 - Corrosion tests in artificial atmospheres - Salt spray tests.

Observations:

- Sharp edges: Ceramic and may other coatings present defective points in very sharp edges son in the industrial processes all edges must be rounded to R>4 mm aprox

SCAR (ISO4628-8:2012 *Evaluation of degradation of coatings. Designation of quantity and size of defects, and of intensity of uniform changes in appearance. Part 8: Assessment of degree of delamination and corrosion around a scribe or other artificial defect.*): Horizontal Scars were made before the sea test to evaluate possible undercoating corrosion evolution and the results have been excellent

- Maximum growth allowance: 8 mm
- Lab results: 2 mm
- Sea test results: 0 mm

Round machined circles were made after the test to evaluate the coating’s adherence.

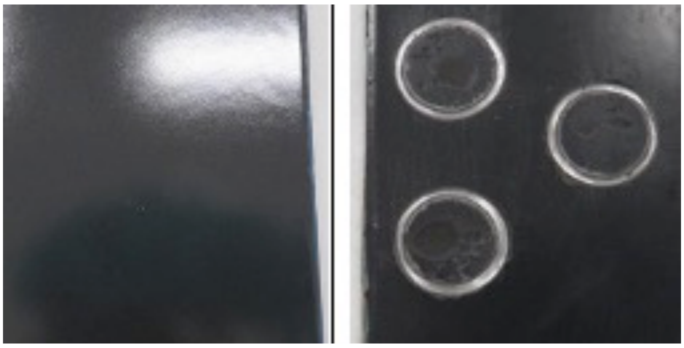
ADHESION - PULL-OFF TEST

There are different test procedures to measure the adherence of coatings to metallic surfaces. All of them give different figures and are thus employed to compare different coating categories

Among the normally used to compare marine paints is the UNE-EN-ISO 4624:2016[1].

Minimum according to this norm is 5 Mpa

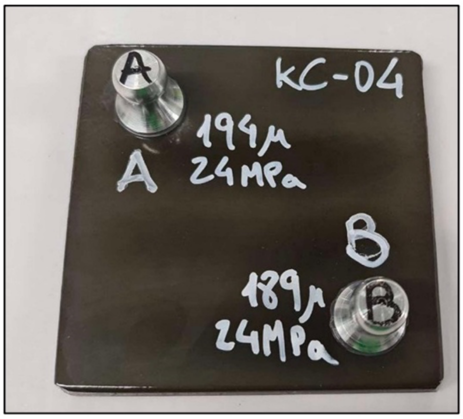
these test always use a perpendicular pull off strength to break the coating
In this norm the pulling part is glued to the coating and the area around that pulling part is machined to separate the pulled part from the rest of the coating as in the picture below



Results:

1. Plates before and after the lab and harshlab test in Tecnalia were no possible as their machine was special to measure LOW adherences as in paints

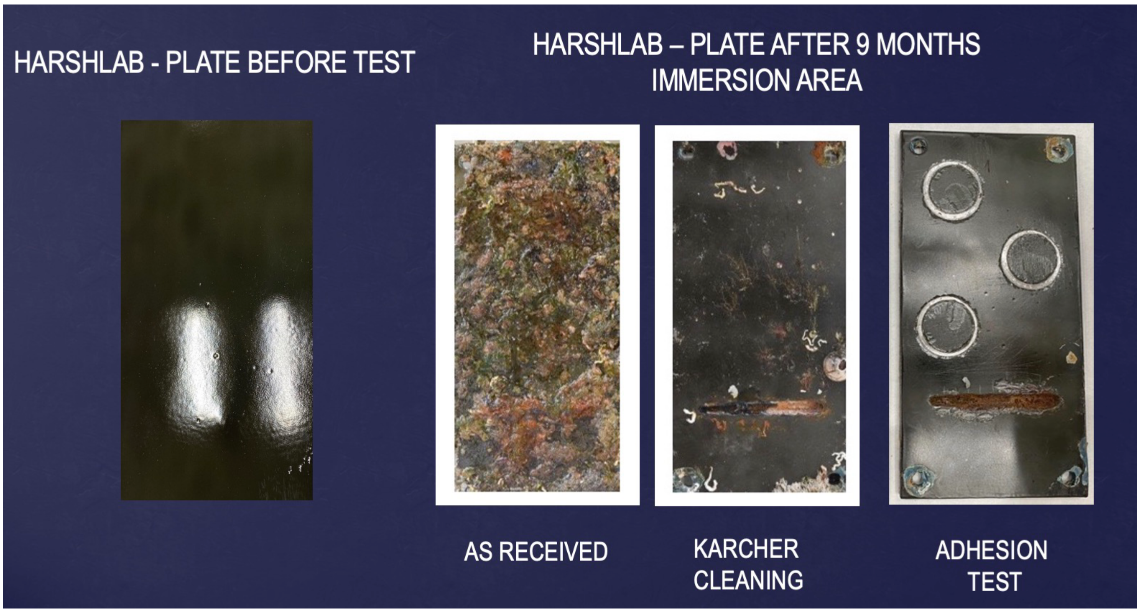
Tested in a Wind tower manufacturer in Bilbao HAIZEAWIND, they stopped the test at 24 Mpa: as that was the max pulling force of the testing machine and the coating WAS NOT BROKEN



The only test that got to break the ceramic by pulling was made 5 years ago at the SHELL Houston Labs and reached the 12.000 psi **(83 MPa)**

FOULING WATER JET CLEANING

FOULING – After 9 months there were algae and some cirripeds over the the plates , mainly in the submerged area.



That fouling was easily cleared with a domestic water jet at 300 bar (Kärcher) and the ceramic was in a perfect smooth condition

As aditional information we have tested similar plates with an ultra high pressure test jet up to 2300 bar at 10 cm distance without any damage to the coating

FINAL CONCLUSIONS

1. **POSITIVE RESULTS IN ALL THE TESTED PLATES apart fropm the marine life fouling which was easily removed and showed no damage to the coating surface**
2. **The main properties of the coating remained unaltered : Shine, continuous vitreous surface , low roughness , thickness …**
3. **There were NO differences between the two vitrification processes: furnace or LASER-VCSEL**