2019 Award Nomination

Title of Innovation:

Ceramic protection for Harsh environments

Nominee(s)

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Category:

Coatings and Linings

Dates of Innovation Development:

(from January 2015 to September 2018)

Web site: https://www.cidetec.es/en/surface-engineering

Summary Description:

A cutting edge technology based on novel ceramic coating protection has been developed for metal components (carbon steel, stainless steel, high and cast alloys), including long and narrow tubes, subjected to industrial extreme conditions. This innovative technology has been developed by CIDETEC side by side with KERACOAT http://www.kera-coat.com/, CIDETEC's spinoff focused on tailor made ceramic formulations initially for the Oil&Gas and PowerGen sectors. This technological approach gives an efficient and environmental friendly solution, protecting components from critical degradation and keeping the energetic efficiency by avoiding fouling and corrosion phenomena.

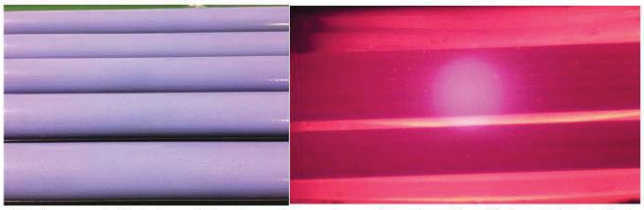
The whole coating process is completely covered due to associated technological services developed to guarantee industrial needs such as on-site welding & repairs in order to avoid weak areas where corrosion mechanism could accelerate degradation processes.

The ceramic coating protection is supported by a suitable thickness (±150 µm) and chemical bonding to the metal substrate, with a glassy and smooth surface avoiding ashes, sub-products and liquids fouling & corrosion degradation. Easy to clean properties, high emissivity, chemical resistance to the most common industrial acids and salts products (hot & cold) and thermally resistant up to 800ºC (metal

substrate temperature) combined with a high abrasion resistance and hardness (64HRc - 840Hv) are also key properties for this ceramic protection technology.

Actually, three industrial successful cases developed over the last 4 years must be mentioned:

- Steam pipes in a WtE boiler.
- Coke calciner heat recuperator.
- Fume condenser prototype at an urban WtE.



6 m long metallic tubes with external ceramic coating placed in a Coke calciner's Heat Recuperator with Vanadate Ashes

Apart from these use-cases, ceramic coating solution can be applied to similar operational processes related to energy production in delayed coke furnaces, overhead condensers, flue gas condensers, steam boilers as flue gas economizers/exchangers with associated hot ash corrosion in coal burning plants, waste heat boilers in sulfuric acid plants as well as in heat exchanger tubes at cooling water temperature, etc.

Full Description:

1. What is the innovation?

An advanced ceramic coating, based on silica-based matrix formulated in aqueous medium, able to increase the durability of metallic components (big size and geometries) installed on industrial facilities working on harsh environments (corrosive medium, temperature, ashes from combustion processes, etc.). The ceramic coating involves a complete application technology specifically developed to give a turnkey solution to the customer, including coating the remaining areas and pieces after installation (welds, elbows, fittings, etc.). This coating technology covers all the whole key points where other competitive technologies cannot reach.

Beside its industrialization feasibility and developed complementary technologies, the most notable feature is related to the enhanced properties that the ceramic coating can offer, supported by some successful milestones achieved in different harsh industrial facilities. In this sense the most remarkable properties are listed as follow:

- Chemical bonding to the metal substrate and glassy Surfaces with very low roughness (Ra: 0.1 – 0.2 µm) -> little or no adherence of fouling.
- Thermal resistance up to 800ºC in the metal substrate.
- Thermochemical resistance to gases and/or salts deposits.
- High Emissivity values (0.83) at 550ºC compared with oxidized steel (0.6).
- Erosion resistance to abrasive particles; Hardness: 64 HRC.
- Water Pressure Cleaning Resistance up to 2300 bars (33,360 psi).
- Specific ceramic formulations for welded areas.
- Chemical Resistance to hot & cold acids (sulfur and sulfate, nitric, chloride, except HF), hot & cold alkalis (except concentrate NaOH & KOH), water hot & steam and high concentration of salt water.

So, this technological solution has been specially developed to fight successfully in most corrosive and “dirty” environments (refineries, petrochemical industry, cement industry and power plants, even off shore wind). In this sense, the most important innovation is to **combine in only one coat**, environmental friendly, three key properties such as **resistance to temperature, to corrosive/abrasive environments and antifouling properties,** adding the feasibility to its industrialization to big components based on metal substrates. All this leads to increase the protection from critical degradation. Thus, as ashes, fluids and generated sub-products (coke, salts, etc.) don’t stick to the coated components new improvements opportunities had been opened by these results:

- Cleaning “shakes” can be reduced if not avoided.
- Thermal efficiency will remain more constant as ash insulation will not grow.

- It could allow designing boilers working at higher steam temperature, reducing the boiler size for the same output and with lower maintenance costs, so there will be an automatic increase of efficiency just by avoiding the loss due to ash fouling.
- A new way to recover the heat from the industrial exhaust fumes, based on already known heat transfer principles (full condensation) but which represents a great step forward apart from being able to provide an alternative energy source, allowing:
    - Extra clean fumes that could even be used in agricultural greenhouses (CO_2, N_2 and water at 35ºC).
    - Recovery of condensate water instead of consuming it (Scrubbers).
    - The condenser acts perfectly as a filter, taking with the condensates more than 60% of the flying ashes, reducing the filters work.

All this mentioned improvements are currently being industrialized successfully and will be described in more detail in section number 4.

2. How does the innovation work?

Ceramic silica-based coatings have been specifically design & developed to provide corrosion protection to some metal substrates (stainless steel, carbon steel, high alloys and cast alloys), resulting from a controlled fusing process of inorganic constituents and designed to form a surface layer over the metal substrate. The conventional coating process involves the preparation of the formulation (starting from the innovative ceramic matrix) by blending raw materials in a suitable formulation to meet the requirements of the coated piece, followed by a pretreatment of the workpiece to be coated (usually sandblasting as a simple step), in order to remove impurities from the metal surface followed the deposition of ceramic formulation on the piece using the most appropriate technology to ensure optimum performance. The most commonly application technologies are spray coating, dipping and flow coating (electrophoretic deposition and powder electrostatic could also be mentioned). Finally a thermal treatment over 700-950 ºC is needed in order to consolidate the ceramic silica-based coating on the metal substrate.

In particular, controlled application processes of ceramic silica-based formulations are a scientific and industrial coating technique to obtain a very smooth surface finishing and excellent edge coverage, even where the access is limited. The appropriate combination between formulation and application technique is known to be effective for the production of functional materials. In addition, redox reactions are the mechanisms that enhance the chemical bonding between ceramic coating and metallic substrate during thermal treatment.

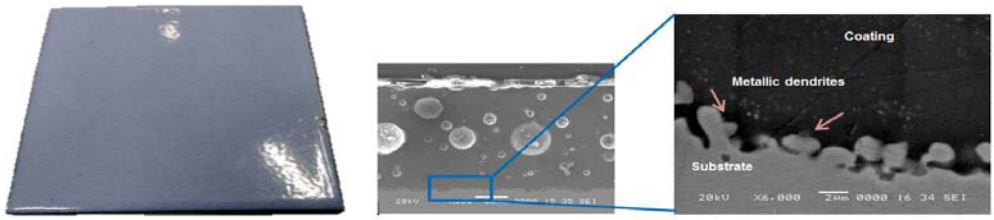
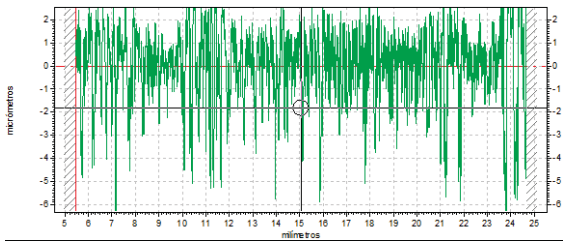
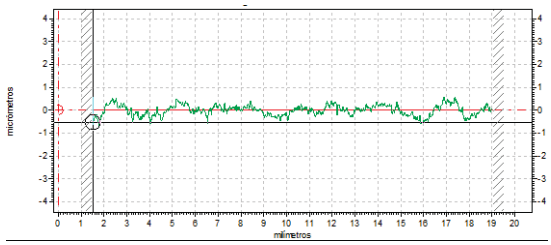


Fig. 1. *Coating applied over 310 substrate and Chemical bonding interface obtained by SEM*

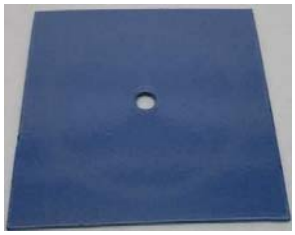
The roughness profile obtained from an uncoated 310H stainless steel sample exhibits Ra and Rz values of 1.18 µm and 5.49 µm respectively, although a coated sample depicts smaller values, specifically 0.18 µm for Ra and 0.96 µm for Rz parameters. The difference of roughness helps to mitigate the adhesion of particles and therefore to improve the anticorrosive behavior.

Table 1. *Roughness results for uncoated samples and ceramic coating*

Uncoated sample	Ceramic coated sample
	

Abrasion test has been done with a TABER Rotary Platform Abrasion Tester according to EN ISO 5470-1 standard. The difference in weight before and after applying 5.000 cycles, gives an idea about abrasion resistance. In this case, 310H stainless steel sample lost 33.6 mg whereas the coated sample missed only 1.6 mg.

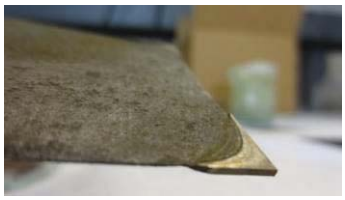
Table 2. *Taber abrasion test results between uncoated vs. coated sample*

	Before Test	After Test
Uncoated sample		
Coated sample		

Thermal shock was evaluated under ISO 2747 proceeding, starting from 550ºC for 30 minutes, after which samples were taken out and quenched in cold water, repeating the cycle each 50ºC until damage is observed in the surface through cracks or superficial defects. Under this protocol, the tests were done at 650ºC, 700ºC, 750ºC, 800ºC with only a loss on brightness but no evidence of superficial damage. Micro-cracks finally appeared at 850ºC.

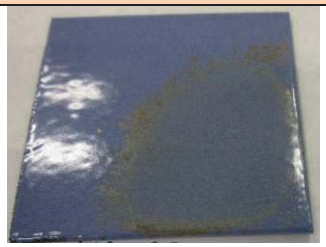
Chemical Resistance to Iron Sulfate was measured over uncoated and coated samples for 24 hours at 75ºC using a 20% Iron Sulfate water solution. Table 3 shows that corrosion signs (material, brightness and roughness loss) were clear over uncoated sample after being subjected to the corrosive solution, where a reddish appearance and even mass loss were also present. However, coated sample appearance remained unchanged after being in contact with the corrosive solution keeping its initial brightness and without weight loss.

Table 3. *Chemical Resistance to Iron Sulfate test results*

Uncoated sample after 24h test		Coated sample after 24 h test
		

Resistance to Sodium Vanadate and Sulphur (V_2O_5/Na_2SO_4; 40/60 weight) was evaluated over two samples (uncoated and coated). The corrosive resistance was analyzed in a furnace at 600°C for 1, 4 and 240 hour. After the test, a noticeable mark was evident onto the uncoated surface, while the coated surface showed no corrosion attack, only a slight effect with the presence of halos and some brightness loss but without changes in the superficial roughness.

Table 4. *Chemical Resistance to Sodium Vanadate and Sulphur test results*

Uncoated sample after test	Coated sample after test
	

Emissivity of the coated sample was also measured using SNEHT method at room temperature and SNHRRT/V1-MIR method at 550ºC. Values concerning operational temperature in a great number of industrial processes (550ºC) is higher (0.83) compared with oxidized steel (0.6). In this sense, the ceramic coating can contribute to increase and homogenize the temperature associated to heat processes, allowing increasing the efficiency.

Once checked the key properties of the coating we move to the associated technologies needed to industrialize this innovative solution to long tubes (inside & outside), components and structures.

As commented previously the aqueous formulation could be applied using reliable technologies (spray and dipping) used for other types of coatings (paints). After removing the humidity from the coating (air or forced by an oven at 50-70ºC) a thermal treatment over 700-950 ºC (10 minutes) is needed in order to consolidate the ceramic silica-based coatings on the metal substrate.

Fig. 2. *Long tubes coated with ceramic coating*

Individual components (tubes and structures) could be supplied completely coated, but in most cases, during the installation in the industrial plant it is necessary to carry out welding processes, threaded, joints, etc., in order to generate the complete structure, so, and always at the customer's request, the part of the component that will be welded or fixed does not coat.

Components surface protection (i.e. tubes) is very important during different shop operations (transport, welding, sandblasting). In this sense, a system has been developed for "on site components assembly", made on hard but flexible plastic, easy to clamp and withdraw. Apart from this, and during joining processes is very important to protect (duct tape) just the border of the coated area.

Once the individual components have been joined, these areas remain uncoated, becoming a critical zone where corrosive mechanisms could be rapidly developed. In this sense, ceramic coating technology has developed a novel system, with associated equipment, to protect with only one coat and without using primer these welded areas. In the same way, ceramic matrix formulation has been adapted, without modifying its inherent properties. This coat, using the equipment specifically developed for this item, can fuse and mix with the previous one avoiding coating transition areas, protecting all the required structure.

As will be commented in section 4, describing the industrial cases where this technology successfully has been developed, we honestly think that this 4 years ago *promising technology* has become an industrial reality supported for the upcoming projects with some key players in the Oil & Gas and PowerGen sectors.

Fig. 3. *Chamfering* operation and *associated equipment to coat welded and joining areas*

3. Describe the corrosion problem or technological gap that sparked the development of the innovation? How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

There is a wide variety of structures and components of different industrial sectors that are exposed to aggressive environments and therefore subjected to corrosion, giving a loss of functionalities that limit their performance shortening their service life. In many cases, especially in fluid lines, corrosion problems are aggravated by the deposition of undesirable substances on the components. This effect is increased by the high temperature present in most industrial processes, sources of generation of gases with high corrosive properties, causing a series of functional problems that imply that important efforts have to be devoted annually to cleaning, maintenance and/or replacement of the components.

In this sense, there is a large number of potential applications where this technological solution can be applied such as power generation boilers, molten salts collectors included in CSP, ash corrosion and fouling in the oil and gas Industry, metal dusting avoidance, fuels production and chemical synthesis industry, combustion fumes condensation, nitric acid condensers, refinery and Petrochem heat exchangers, overhead Sulphur condensers and heat recovery systems in general. Due to the proven resistance to hydrogen migration (ceramic is a barrier) another foreseen R&D line would be to use it against hydrogen embrittlement.

With this scenario, it is understood that one of the most important challenges is related to the development of materials and surfaces that could provide a high resistance to the operational work environment: temperature, corrosion, fouling/scales.

As commented in section 2 and further demonstrated it feasibility in section 6 (industrial successes), the coating technology presented could solve the gap related to the limitations associated to the current available technologies in the following form:

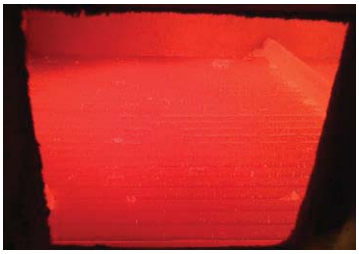
Currently solutions	Ceramic coating Innovation
Recommended steels with a very limited life cycle, which forces the plant to stop for its scheduled replacement in order to avoid breakages, etc., with the associated economic loss.	Surface protection with enhanced thermochemical properties (section 2).
Use of alternative alloys: Use of high alloy steels with enhanced resistance (with copper, aluminum, silicon, chromium, molybdenum, tungsten, niobium ...) but very expensive depending on the application.	Surface protection with enhanced thermochemical properties (section 2). Possibility to use steels with a low grade supported by the ceramic coating technology.
Modification of the process conditions: Reduction of the causes of the problem by modifying, as far as possible, the parameters of the production process.	Due to excellent properties, even is possible to increase process conditions and improve process efficiency.
Surface treatments: Certain surface treatments (mechanical or chemical) can mitigate the appearance of defects associated with the attack on the metallic substrate.	Surface protection with enhanced thermochemical and roughness properties (section 2).
Thermal spray and its variants (HVOF, Plasma Spray, etc.) are a reliable technique to obtain protective coatings over metal substrate that could withstand severe thermal and corrosive conditions. Anyway, some limitations are present: great roughness that involves a further and expensive machining and/or sealants application, a low mechanical bonding to the substrate as well as the difficulty to apply the powder materials in some closed areas (i.e. long and narrow tubes).	Chemical bonding to the substrate (better adherence). No need to post-treatments. Better industrial feasibility. Smooth and non-adherent surface.
Ceramic paints (high content of ceramic particles using a polymer/resin to link them forming the final coating) but with a low thermal resistance in long periods of use.	Chemical bonding to the substrate (better adherence). Higher thermal, chemical and antifouling properties. Higher abrasion resistance and much higher hardness.
Diffusion alloys have a reduced resistance to some aggressive chemical agents	Higher chemical resistance.

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.

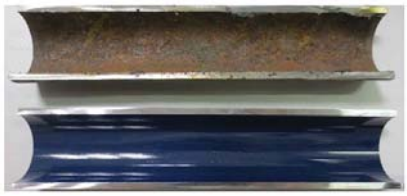
The innovation has been tested and validated in laboratory, as described in section 2, and then, with the entire associated technology ready to industrialization, offered and proved successfully in three industrial use cases:

- Three years of testing in the **WtE boiler** (Spain) under real service conditions (T_{Fumes}= 720 °C; T_{Steam}= 330 °C; T_{Steel}= 350 °C; P= 100 bar) has allowed concluding that ceramic coated prototypes present excellent high temperature corrosion and thermal resistance to oxidation with excellent substrate-coat bonding under thermal stress conditions compared with non-coated DIN EN 1.5415 substrate. http://www.kera-coat.com/upload/secciones-publicas/2017/09/27/power-generation-boilers_original.pdf

- A whole **coke calciner heat recuperator** (USA) S31009 grade tubes, which usually present a very short life (less than 12 months), with ceramic coated tubes was built, and after 12 months in operation, visual inspection reports that none of the tubes has been corroded. The results obtained in the coke calciner show a high performance industrial solution to avoid hot ash corrosion processes associated to the presence of ash deposits containing vanadium oxides and sodium sulfates. https://www.cidetec.es/es/top-achievements-3/ceramic-coating



- A prototype of a **flue gas condenser** (Spain) based on internally coated tubes was developed as a *new way to* recover the heat from the industrial exhaust fumes. The condenser was tested in a WtE plant after filters with very positive results. The condensed water was very acid (PH 3.5), showing that the cleaning effect of the fumes was very significant and discovering that the condensed water acted as a particle filter. In the figure can be observed the internal finishing comparative after six months working fume condenser (non-coated and silica-based ceramic coating). Associated on-going studies are focused on the potential internal applications of fumes after the exchanger (sensible heat might be used to generate electricity via ORC, district heating or cooling, etc.) and the quality of condensates for water recovery and treatment design; a big amount of condensed water could be recover, reducing water consumption. https://www.cidetec.es/es/top-achievements-3/formulaciones-ceramicas



5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?

Ceramic coating protection is specifically design to extend the lifetime of some critical industrial installations subjected to extreme corrosion environment, including high temperature and pressure processes. Direct benefits could be listed as follow:

- Cost savings referred to O&M procedures.
- To use ceramic protected low grade steel materials as opposed to current ones.
- To contribute to reducing harmful emissions related to industrial exhaust fumes (flue gas condenser use case described above).

- To increase some industrial processes efficiency due to the possibility to improve operational working parameters (temperature, pressure)

In addition to this, the innovation presented, just like others coating technologies, can be also monitored to control and predict associated corrosion.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?

The innovation is commercially available for 2 years at a small scale and strongly supported since 2018 from a solid and complementary industrial value chain, with a joint experience in previous projects. CIDETEC Surface Engineering, with a long-standing experience in the design and development of ceramic coatings for harsh industrial applications, supports the scientific and technological axis of the innovation along with TORRECID a manufacturer of ceramic materials. Industrial services and products are provided by two engineering companies: KERA-COAT, focused on the design of advanced ceramic formulations and TUBACOAT, with a great expertise in the application and validation of ceramic systems for tubes that involves a technological leap compared to the solutions currently used.

Currently challenges are preferably focused on three improvement areas:

- GO INDUSTRIAL: TUBACOAT new plant will be on stream before 2018 ends. This plant will coat tubes (inside & outside) up to 11m.
- To increase working properties of the ceramic at 900ºC in metal.
- Adapted thermal technologies to consolidate ceramic coating in big surfaces -> On-going project.

Fig. 4. *CIDETEC Surface Engineering Institute and TUBACOAT new Plant*

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

No patents have been registered.

Otherwise, some trade secrets have been deposited at an intellectual property office in Spain, including all the relevant information of the technological innovation described in this document.