NEW COATINGS FOR THE FUNCTIONALIZATION OF ENAMELLED SURFACES

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Introduction

Ceramers are hybrid materials made of inorganic structures interconnected by polymers, with properties of ceramics (thermo resistance, chemical resistance, anti-scratch behaviour, stiffness) and polymers (elasticity, hydrophobicity).
In the past they find out a broad application in aluminium pots & pans field as anti-sticking coating with high scratch and abrasion resistance.
New developments of the coating allow application on different kind of supports, normally pre-treated in a way to generate a certain roughness on their surface:

- Aluminium and aluminium alloys, laminated or press-fused, chemically pre-treated and slightly sandblasted.
- Steel and stainless steel, pre-treated by degreasing and slightly sandblasted or pickled.
- Aluminated steel, chemically pre-treated.
- Enamelled steel, coated with a final layer of specific hard ground enamel.
- Brass, pre-treated by degreasing and slightly sandblasted.

Ceramers were applied on the support by two layers with a relatively low pot life, but new developments now allow the application by one single layer with a longer pot life (24-48h).

The coating is made normally by 3 components:

- Water phase, containing all inorganic components included nanoparticles and pigments.
- Organic phase, containing the hydrophobic components.
- Catalyser, to speed up the reaction between the other two phases.

Modifying the water and organic phase content it's possible to get more anti-sticking or more thermo resistant coatings coming to interesting compromises.

As up mentioned, the coatings have been adapted to different kind of supports to satisfy different application requirements.

In particular the application on enamelled steel guarantee the functionalization with anti-sticking properties of a relatively cheap support resistant to temperature, oxidation and corrosion, particularly adapt for usage in objects used at high temperatures, for instance pots & pans and cookers.

The support: hard ground coated enamelled steel

In most cases steel is a relatively cheap materials used to make a number of different objects. Steel has to be protected in general from oxidation and corrosion especially when used at high temperatures. It's known that enamel is an extremely heat and abrasion resistant coating able to protect steel and increasing its performances.
Enamel is a material particularly suitable to food contact, even if sometimes food residuals could stick on it. It's possible to change its surface tension, giving an anti-sticking behaviour, by a functionalization of its surface.
The application of a ceramer on top of it gives to the object a good anti-sticking property joined with a good scratch and abrasion resistance also at relatively high temperatures.
Ceramers have no adherence on a simply enamelled surface: it is too smooth and do not have enough roughness to guarantee a physical grip.
We tried to slightly sandblast the enamelled surface, but this mechanical process hampers the enamel bubble evolution. After application and curing of the ceramic coating many surface defects, like dimples and black spots, could occur on the surface.

A viable way is the application of a specific hard ground on the enamel surface. This enamel is hard enough to guarantee an enamel surface rough and slightly porous, but able to be adherent to the base coat enamel.
The developed formula is for wet spray application in 2c/2f on fired enamel.
It's necessary to apply just 30 – 40 µm of hard ground enamel on fired base coat enamel, dry it and fire at the common enamel firing temperatures.
The aspect of the hard ground should be rough and slightly porous, a drop of water should be absorbed by its surface after few seconds.
The porosity guarantees a certain absorption of the coating after application and the roughness helps physical link of the coating to the hard ground surface.
The ground is made by hard materials and the roughness of the surface guarantees a better scratch and abrasion resistance of the coating.
This process could be particularly indicated for, but not limited to:

- Baking trays.
- Oven panels.
- Steel pots & pans.

The coating

The first use of ceramers was for cookware, where the scope of this coating was to replace Teflon, in order to eliminate the use of PFOA, known for its toxic and possibly carcinogenic effects.
Coatings produced using sol-gel technology show ceramic features combined with polymeric ones. Compared to PTFE, sol-gel coatings are harder and can function at higher temperatures (up to 500°C) with good abrasion and surface resistance. Besides they have good initial release, high gloss and good stain resistance.
It's possible to modulate the anti-sticking and thermo-resistance properties working with the composition : the most anti-stick coating is less resistant to temperature and vice versa.
Ceramers can be made in a variety of colours. They maintain colour at high temperatures. This is not the case with PTFE coatings and the reason why most are black or grey.

Sol-gel systems are typically multistep systems.
Each coating can have 2 or more components to be mixed to achieve the final result. So, for example, a one-coat sol-gel coating will have 2 or more components to mix to achieve that coating. For a two-coat, each layer of the coating has multiple components to mix, separately for each layer. The number of packs per layer varies from product to product. Generally 2 packs systems require a full 24 hours of mixing, while the newer sol-gels are made of 3 packs systems which require as little as 4 hours. The product used for this research study is made of one-coat layer made of 3 packs system.

The water phase contains titanium dioxide nanoparticles, in form of water suspension, a black pigment, a refractory micrometric powder and the anti-sticking component.
The organic phase contains silanes and alcohol.
The third phase is the catalyser, an organic acid.
On ceramer formulations a request of patent n° **FI2011A000038** was made in 2011.

The preparation process is a fundamental passage in the sol-gel coating application. The process involves: Activation, Filtration, Surface Preparation and Application. Prior to activation, the individual components must be mixed thoroughly since the fillers tend to settle. Once properly mixed, components are combined in specific ratios in a mixing vessel for a specific time. During mixing, the chemical reaction causes an increase in the temperature of the mixture. Before application, it is necessary to filter the mixed product.

Generally the chosen substrate needs a specific preparation, different on the basis of the substrate material.
The most common substrates used with sol-gel coatings are aluminium and stainless steel. As with any coating, surface preparation is critical and must be done properly to ensure adhesion. First, the pans must be degreased/cleaned to assure the surface is free of oils. Any oil or grease can contaminate the blasting material and interfere with adhesion, especially with repeated use of the material.

Most pans to be coated with sol-gel have the surface grit-blasted, which roughens the surface and provides more “teeth” for the coating to grab on to. If the surface is too smooth, it can negatively affect both adhesion and mechanical performance. If the surface is too rough, it can cause the coating to be drawn into the surface profile, resulting in a dry, rough finish. In the case of enamelled steel reported in this article, no specific pre-treatment was made.

With sol-gel coatings, there is a specific time by which the activated and filtered coating should be applied to achieve maximum effectiveness. The coatings are applied via common spray equipment. Sol-gels must be applied only to preheated parts that maintain about 50-70°C throughout the spraying process. If parts are not heated and kept at this temperature, the coating could sag, cause wetting defects or dry spray. It’s necessary to apply just 25 – 35 µm to ensure proper performance. A too high thickness can cause bad adhesion and following detachment of the coating. At the end the substrates are cured in conveyor or batch oven.

Application

A three components black coating was prepared for this study. The components were mixed for 4 hours and the final mix was filtered before spray-gun application. The substrates were pre-heated at 50-60°C before application. After application, the substrate were dried at 250 °C for 20 min. In the below photo are reported the uncoated substrate and the coated one.

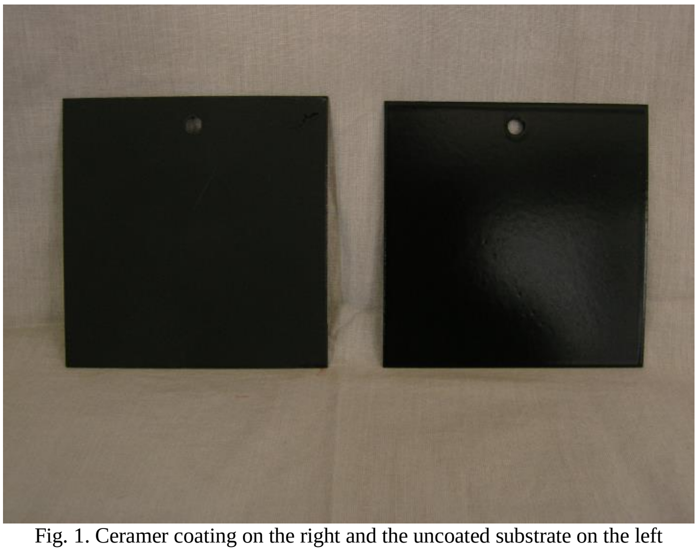


Fig. 1. Ceramer coating on the right and the uncoated substrate on the left

Experimental data

Morphological characterization

The support of enamelled sheet was characterized morphologically by electron microscopy field emission SEM-FEG. From the pictures it can be noted the different layer on the steel surface. It is possible to evidence the first porcelain enamel and the second one. On this layer, we note the ceramic layer. In the picture below, the three different layers are evidenced by the micro-analysis spectra.

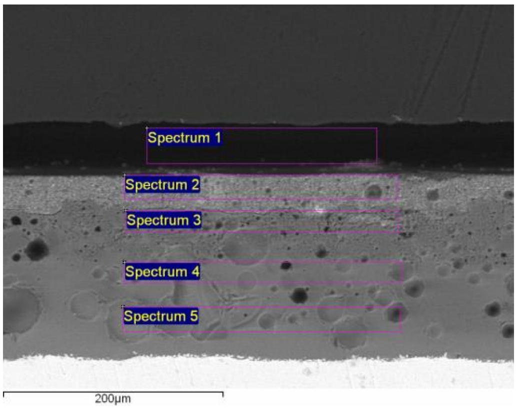
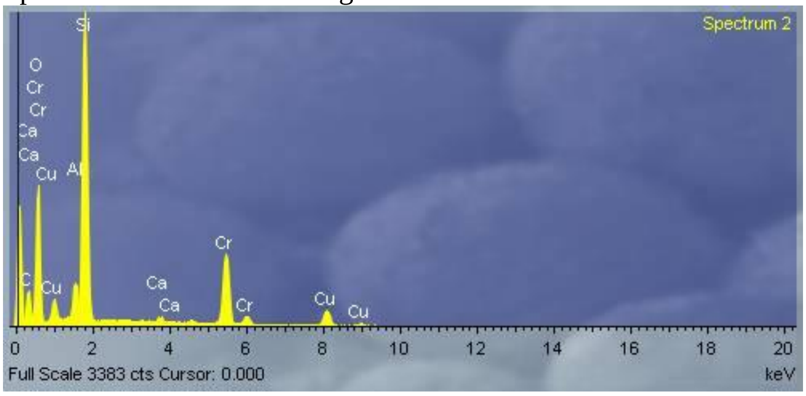


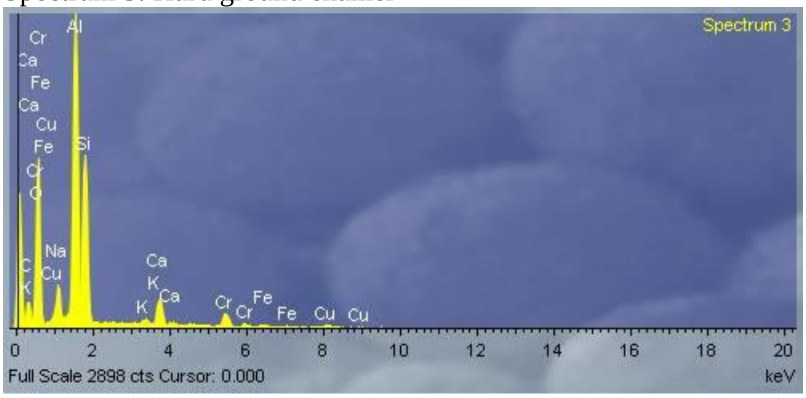
Fig. 2. Ceramer coating 250x BS

Spectrum 2 : Ceramic coating



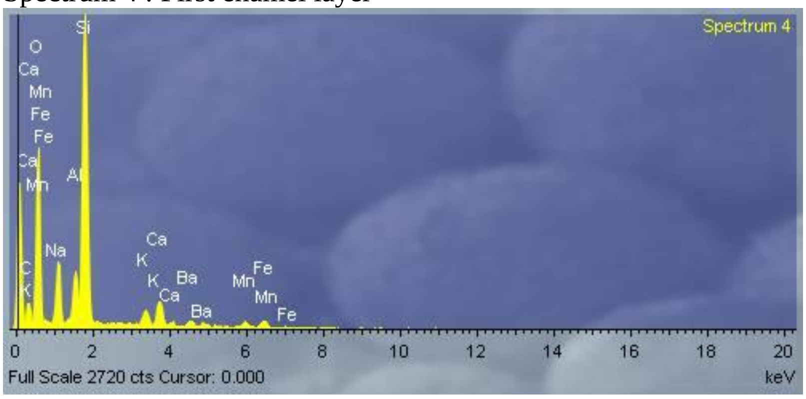
Cu and Cr are well evident. They are pigment elements. Also Si peak is marked, due to the high presence of this element in the formulation.

Spectrum 3: Hard ground enamel



The rought and porous structure of this layer is obtained using hard materials rich in Si and Al like evidenced by the peaks.

Spectrum 4 : First enamel layer



The first enamel layer should be chosen having care that it has a limited interference with the hard ground layer.

From the SEM images, the thickness coating was measured. Also the image show the good adhesion between the hard ground and the ceramer coating.

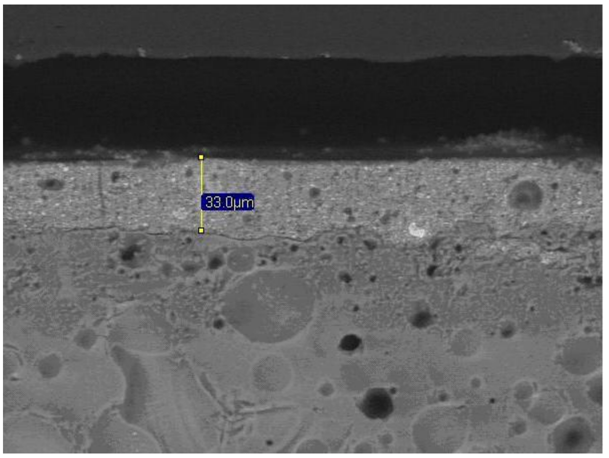


Fig. 3. Ceramer coating 250x BS

Heat resistance of anti-stick properties

The anti-sticking properties were evaluated by water contact angle measurement. The initial value was calculated by repeating measurements on three different samples. The water contact angle was measured using a pocket goniometer (PG-X from Fibro System) and six measures were made on every sample. An initial value of 89.6 ± 2.1 was measured.
The anti-sticking properties were tested versus heat resistance. The coating was submitted to repeated thermal cycles at two different temperatures, 250 °C and 400 °C, and the angle contact was measured after every cycle.
250 °C and 400 °C were chosen because are one is a representative working temperature of a traditional oven (250 °C) and the other one is an average cleaning temperature of a pyrolitic oven.
In the following graph the contact angle trend for the two different temperatures is reported.

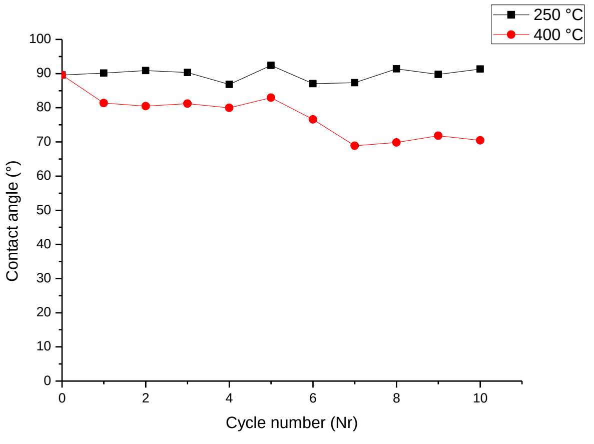


Fig. 4. Contact angle values trends for 250 °C and 400 °C

It is evident that the anti-sticking properties show no changes after 250 °C treatment. Indeed at 400 °C the contact angle value tends to decrease and a loss in hydrophobicity means a loss of anti-stick properties, even if the value decrease is not so marked.

Conclusions

It was possible to design a specific hard ground enamel coating that allow the adhesion of an hybrid ceramic coating onto an enamelled surface. The system has been characterized and tested to measure it's suitability to have a good anti-sticking performance in conjunction with an excellent heat resistance. Repeated heating cycles in normal oven working conditions show a good resistance of the coating film in terms of hydrophobic characteristics. This fact, combined with the interesting scratch and abrasion resistance of this products leads to a new class of non toxic, easy to clean coating for several applications.