

STUDY OF INTERFACE AND SURFACE PROPERTIES IN MULTILAYER CERAMIC SYSTEMS

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1. ABSTRACT

The generalisation in recent years of the use of inkjet technology for ceramic tile decoration has led to in-depth study of the technology's operating principles and process variables. These notably influence the characteristics of the deposited layers, as do the physico-chemical properties of the applied inks and the glazes that serve as ink substrates. The issues associated with this combination of factors become thornier when inks with complex formulations designed to obtain special effects are involved.

This study addresses the characteristics of the interface that is generated on applying an ink on a certain type of glaze, as well as the surface properties of the end product. The study also seeks to determine the influence that certain process variables have on these interface and surface properties, with a view to maximising the development of the targeted effect and thus achieving more precise control of the most significant factors.

2. INTRODUCTION

The incorporation of inkjet technology into ceramic tile decoration has entailed a great aesthetic and technical breakthrough, as the innovation possibilities afforded by the technology go far beyond just colour decoration while also posing important challenges, owing to the singularities of the technique (extremely fine particle size, constraint on the applied weight, etc.), which largely condition decoration with special effects, including the sought-after metallic effect.

Ceramic tile decoration with a metallised appearance, using no noble metals in the decoration composition, was developed in the first decade of the 21st century. Glaze compositions that had been used in traditional applications, mainly waterfall glazing or airbrushing, were involved, whose chemical composition was fundamentally characterised by the presence of iron oxides and phosphorus. In order to transfer this type of product to *inkjet* decoration, the main problem lay in the thickness of the layer needed to obtain a quality metallic effect, which was at least about 250–300 g/m², this being impossible to obtain by digital printing, at least with a reasonable number of printhead bars. To overcome this problem, Color Esmalt filed a patent in 2012, which has since then been awarded, ES 2 396 399 B2 [1], for the obtainment of metallic effects on ceramic substrates by *inkjet* printing. In this case, the metallic effect is obtained by a superimposed application of glaze and ink with an appropriate chemical composition, such that the set of oxides required to obtain the metallic gloss is distributed between both applications. Logically, owing to its colouring effect, iron oxide is used in the ink application, together with phosphorus depending on manufacturing alternatives, the remaining elements being left in the glaze formulation.

The first research into P-Fe glass-ceramic glazes conducted by J. Ma Rincón [2], and in subsequent studies [3-7], already established the importance of the surface crystallisation of certain phases such as iron phosphates, mixed alkali and alkaline earth phosphates, and haematite nano-crystals, the last being responsible, according to Rincón, for the metallic effect of this type of glaze. It is evident that the appearance and the chemical formation and dissolution reactions of these crystalline species largely depend on the chemical composition of the glaze composition and the thermal cycle used, essentially the cooling cycle. However, no study was found in the literature on the obtainment of glazes with a metallic appearance by *inkjet* application of a pigment rich in iron oxide on a glaze with an appropriate composition.

3. OBJECTIVES

This study pursued two basic objectives:

To physically, chemically, and microstructurally characterise the glazes obtained by the *inkjet* method, focusing in particular on the interaction between the different layers making up the glaze, for this purpose studying the transverse concentration gradient and level of ink penetration, which plays a key role in the aesthetic appearance of the piece.

To optimise the process variables chosen as significant, described below in the paper, in order to foster the metallic effect, for this determining their influence on the resulting glaze interface and surface properties.

4. EXPERIMENTAL

The glaze and engobe compositions were prepared from frit and other crystalline raw materials by wet milling. The ink was prepared according to the appropriate technical specifications for application in DIMATIX 1024 and XAAR 1002 printheads. The standard conditions of the reference product, used as starting point in this study, are summed up in Table 1.

Reference sample	Glaze PSD		Glaze layer thickness	Coating factors		Thermal cycle
	D_{50} (μm)	D_{90} (μm)	Solids weight (g/m^2)	Resolution (dpi)	Weight (g/m^2)	Porcelain tile
STD	9.4	38.6	300	800	21.6	1195°C

Table 1. Standard values of the process variables that were modified to study their influence on resulting tile aesthetic appearance.

With a view to optimising the metallic appearance, various experiments were conducted, modifying the reference conditions. In the case of the glaze, special attention was paid to a wide particle size distribution (PSD) range in order to study the influence of PSD on ink penetrability and final appearance. The ink was applied by inkjet technology with different resolutions, from 400 to 1200 dpi, to thus obtain a different weight per unit surface area. A porcelain tile body was used, with thermal treatment according to a standard firing cycle, whose process variables were in turn modified, based on variations in an industrial production cycle to thus study their influence on the resulting ceramic tile finish.

In order to be able to evaluate the metallic effect of the pieces, the most important characteristic was the change in luminosity and gloss when the sample was observed from near specular angles to far specular angles. The $CIE L^*a^*b^*$ chromatic coordinates were therefore obtained with a diffuse reflectance spectrophotometer. These were used to calculate lightness (L^*) and chromaticity (C^*_{ab}) of the fired glazes, in order thus to define the reddish, metallised, or blackened appearance of the pieces. Gloss was determined with a reflectometer, with incident angles of 20°, 60°, and 85°. With a view to establishing a quantitative criterion that allowed the positive or negative influence of each variation in the study variables to be reflected, a metallic gloss index, θ_M , was defined from the following equation:

$$\theta_M = \Theta_{60} - \Theta_{85} \quad \text{Equation 1}$$

where θ_M represents the corresponding difference in gloss for incident angles of 60° and 85°, measured in gloss units (GU).

Surface and transverse characterisation, from a microstructural viewpoint, was performed by scanning electron microscopy (SEM), observing and photographing sample topography and composition with the backscattered electron signal under high-vacuum conditions. To determine ink penetration depth and the interaction between the different layers, a cross-sectional cut was made, generating test piece cross-sections that, after embedding and polishing, enabled the composition profiles to be studied at different distances from the surface, taking EDX spectra of $1 \times 35 \mu\text{m}^2$.

Finally, coating chemical composition was analysed with an energy-dispersive X-ray microanalysis (EDX) instrument connected to a microscope. To obtain a representative value of the composition, analyses were performed on ten areas of 1 mm² per sample, selected at random. Note that, in the case of the surface analyses, the electron beam penetration, albeit reduced (of the order of 1 µm), was considerable so that the analysis obtained did not correspond exactly to the irradiated surface but to a very thin layer. Nevertheless, for the sake of simplicity, the term surface analysis will be used hereinafter for what was in fact analysis of a thin surface layer.

5. RESULTS

5.1. CHARACTERISATION OF THE STANDARD APPLICATION

5.1.1. SURFACE STUDY FOR CHEMICAL AND MICROSTRUCTURAL CHARACTERISATION

In the surface characterisation of the sample, Figure 1 shows, at low magnifications, diffuse areas with an irregular shape and light colour (surrounded by other darker ones) in which different types of X-shaped (1) and dendritic (2) crystals can be distinguished, whose composition consisted of a core with a high iron content and branchings, fundamentally of iron and phosphorus, as well as isolated iron-rich polyhedral crystals (3).

On observing the light areas at higher SEM magnifications, groups of glossy white particles uniformly distributed throughout the surface can be distinguished. EDX analysis revealed that many of these exhibited high iron and phosphorus contents. In contrast, in the dark areas, the dendritic crystals integrated in the matrix were enriched with aluminium, silicon, and sodium.

The chemical characterisation, in compositional terms, determined by EDX is detailed in Table 2. It may be observed that the interaction between the ink, with a high iron oxide content, and the glaze led to surface enrichment of phosphorus, alkalis and alkaline earths, while zirconium and silicon decreased noticeably. This behaviour stemmed from surface crystallisation of the mixed phosphates and iron mentioned above.

STANDARD	R ₂ O/Al ₂ O ₃	RO/Al ₂ O ₃	SiO ₂ /Al ₂ O ₃	P ₂ O ₅ /Al ₂ O ₃	Fe ₂ O ₃ /Al ₂ O ₃	ZrO ₂ /Al ₂ O ₃
Coating	0.57±0.02	0.51±0.02	3.95±0.02	0.76±0.02	0.49±0.01	0.16±0.04
Glaze	0.49±0.01	0.28±0.01	5.19±0.04	0.53±0.04	-	0.38±0.08

Table 2. Comprehensive chemical composition, determined by EDX, of the glaze and the coating surface expressed as a molar ratio (mole oxide/mol Al₂O₃).

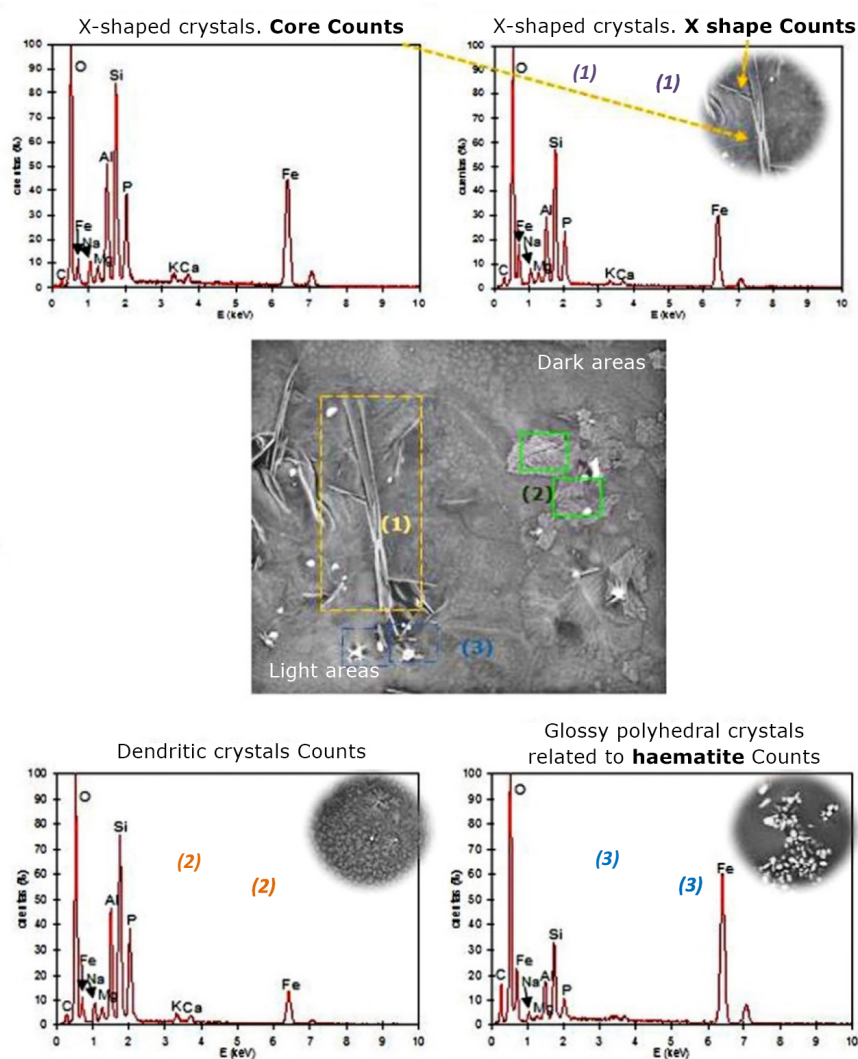


Figure 2. Appearance and composition of the standard sample surface.

5.1.2. CROSS-SECTIONAL STUDY FOR INTERFACE ANALYSIS

Examination and analysis of the composition profile revealed an interaction between the oxide composition of the ink and the glaze (Figure 2), which varied depending on the weight of the ink deposited in the surface layer, therefore modifying the aesthetic properties of the piece. This evidenced the importance of iron diffusion and of the ink penetration depth, and of glaze characteristics (porosity and physico-chemical properties), and hence of the study of the transverse composition in the modified glaze samples.

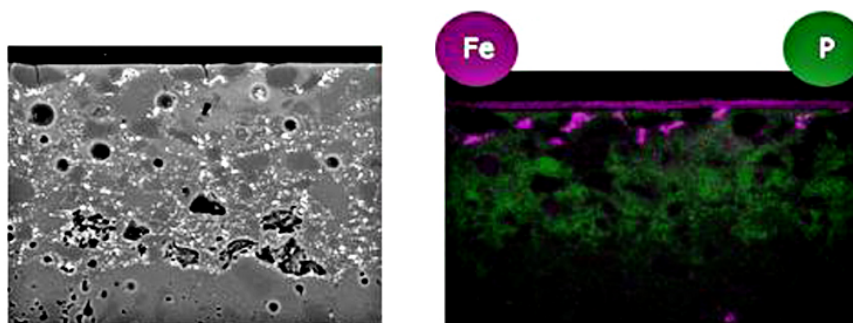


Figure 2. Appearance and composition of the standard sample surface through the line profiling or mapping technique at x1200 of the SEM.

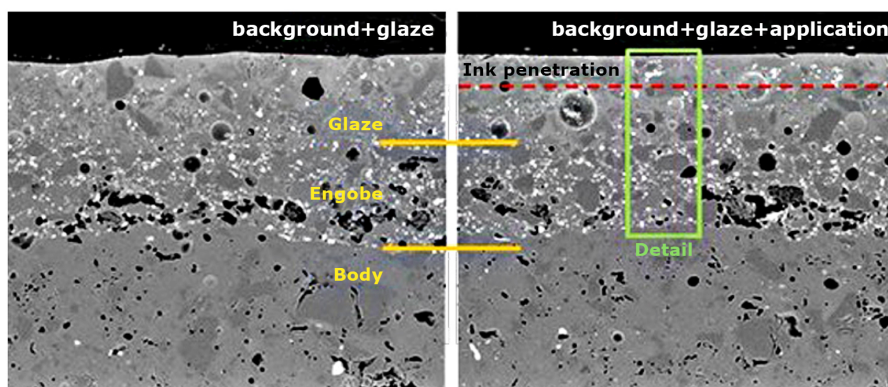


Figure 3. Cross-section of the standard sample at x800 of the SEM.

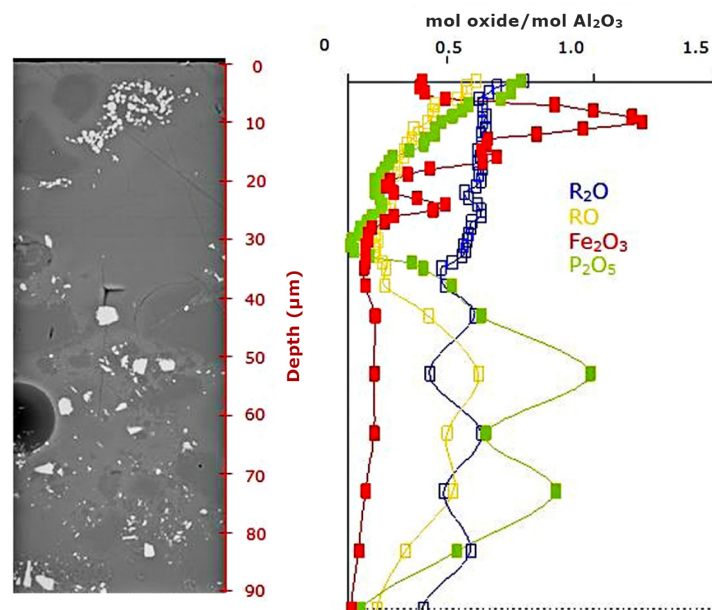


Figure 4. Detail of the standard sample composition profile at x8000 of the SEM.

The interactions between the two layers led to:

- Enrichment of phosphorus, alkalis, and alkaline earths in the proximities of the coating surface, which as noted above was due to phosphate crystallisation.
- Ink iron oxide penetration to depths of about 30 μm , forming haematite crystal agglomerations that were distinguished in the profile by the two peaks corresponding to iron oxide. This penetration occurred by ink suction through the glaze pores. Beside this type of transport, it can also be observed that the partially dissolved iron in the glaze diffused to greater distances (60–90 μm).
- The oscillation of the oxide values throughout the composition profile was due to the heterogeneous nature of the glaze, such that when the presence of quartz, alumina, and zircon particles or of iron oxide agglomerations was detected, the percentage of the other oxides obviously decreased. With a view to palliating this phenomenon, the composition of the glassy phase was determined at different depths, it being verified that except at distances of less than 10 μm , the glassy phase composition was practically homogeneous.

5.2. INFLUENCE OF THE OPERATING VARIABLES AFFECTING THE COATING SURFACE COMPOSITION

With a view to determining the influence of the physico-chemical characteristics of the surface resulting from the interaction between the ink and the glaze on its aesthetic appearance, a series of glazes were prepared modifying the inkjet printing resolution of the metal ink, the particle size distribution of the glaze that served as a substrate, and the firing cycle, such that the resulting surface displayed a different chemical, mineralogical, and structural composition. To quantify the variation of surface aesthetic appearance on altering the surface composition, the chromatic coordinates and gloss were measured. The results and analyses are set out in the following sections.

5.2.1. RESOLUTION OF INK APPLICATION BY INKJET TECHNOLOGY

The modification of *inkjet* printing resolution directly affected the applied ink weight and, consequently, noticeably modified coating appearance with regard to both gloss (Table 3 and Figure 5) and colour. These changes were mainly related to dissolution reactions (undissolved pigment quantity in the glaze) and re-crystallisation.

Reference	Coating weight (g/m ²)	Molar ratio P_2O_5/Al_2O_3	Molar ratio Fe_2O_3/Al_2O_3	θ_M (GU)
STD -1	8.30	0.68 ± 0.03	0.40 ± 0.04	13.1
STD	16.6	0.76 ± 0.02	0.49 ± 0.01	70.9
STD +1	21.6	0.82 ± 0.02	0.55 ± 0.04	110.8
STD +2	35.0	0.77 ± 0.03	1.08 ± 0.03	86.3

Table 3. Variation of coating composition and appearance according to printing resolution.

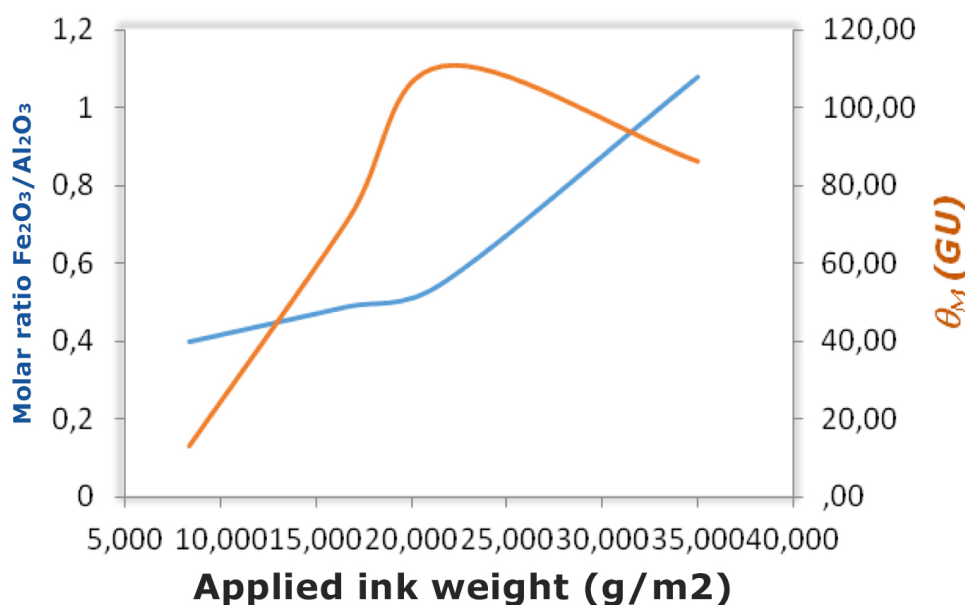


Figure 5. Correlation between glaze gloss and applied ink weight.

The results indicated that there was an optimum level of ink at which the quantity of iron in the glaze was appropriate for generating a surface densified by re-crystallisations in the glaze that maximised the metal effect. Beyond this point, a saturation began to develop that decreased reaction efficiency, thus reducing the targeted metallic effect.

5.2.2. GLAZE PARTICLE SIZE DISTRIBUTION (PSD)

Several particle size distributions were prepared by modifying the milling conditions, without varying the formulation of the standard sample, in order to study the influence that this variable had on glaze permeability and ink penetrability and, consequently, on the surface characteristics relating to the aesthetic appearance to be evaluated.

The above led to a change in aesthetic appearance as ink weight increased (stemming from the resolution used) for each glaze particle size distribution, shifting from non-metallic reddish tones (ink shortage) to a graphite-like appearance (saturated ink), crossing through an area with a glossy metallic effect, Figure 6. However, in the case of a distribution that was too fine, there was no optimum effect development point.

The above led to a change in aesthetic appearance as inkjet ink weight increased per surface area (stemming from the resolution used) according to the different glaze PSDs.

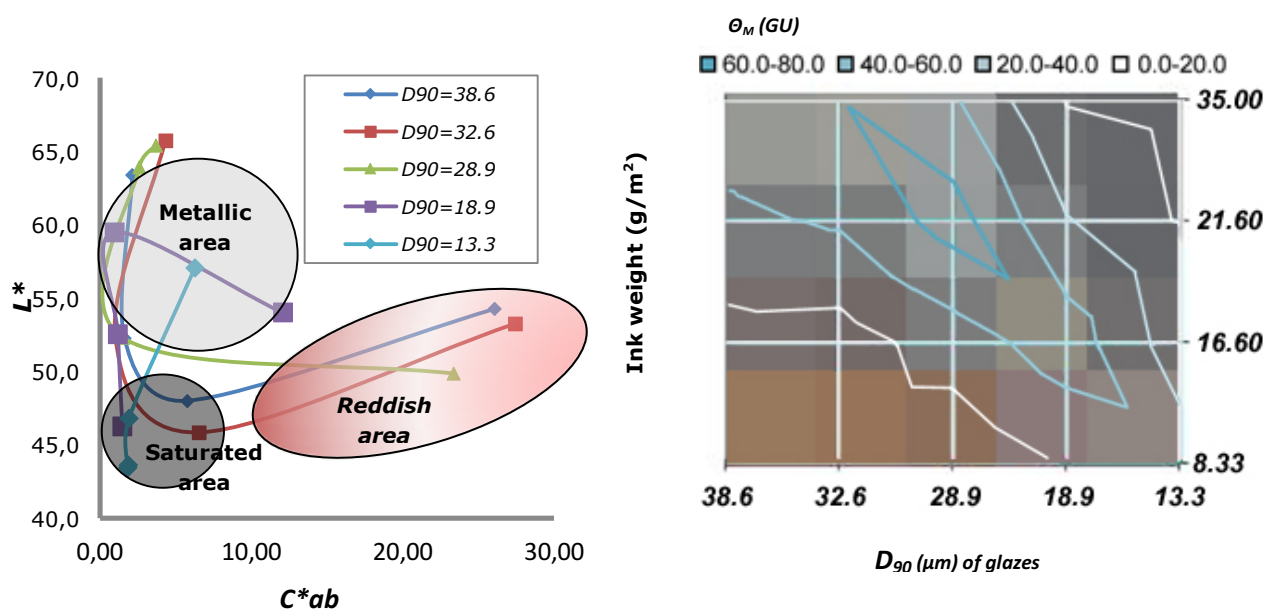


Figure 6. Evolution of gloss and the chromatic coordinates at different particle sizes according to ink weight.

Figure 6 shows that, at a higher glaze PSDs with little ink weight, a non-metallic reddish tone and low gloss index were obtained but that, on adding a larger quantity of ink, the aesthetic properties improved approaching the area with a glossy metallic effect. However, at finer distributions, the area with a metallic effect was reached using less ink than in the case of the coarse distributions, though the transition from the reddish appearance to the saturated (graphite type) appearance was then attained sooner with this type of distribution. The medium sizes were therefore deemed the best because the aesthetic appearance of the fine glaze distributions was more sensitive to the increase in ink weight and, with little variation, the change was more pronounced.

This phenomenon depended on ink particle size, glaze particle size distribution, and the physical properties of the fluid medium (surface tension and viscosity). The influence of glaze particle size distribution stemmed from the fact that, as the particles became finer, the ratio of the average glaze/average ink particle size

decreased, reducing ink penetration, as observed in Figures 7 and 8. As a result both the metallic effect and ink saturation were reached at a lower iron concentration, as was evidenced in Figure 6. Consequently, if the coating layer did not penetrate sufficiently for the reaction to take place at the interface, the effect was not achieved, though with low ink weight the properties improved with relation to other, coarser glaze particle size distributions.

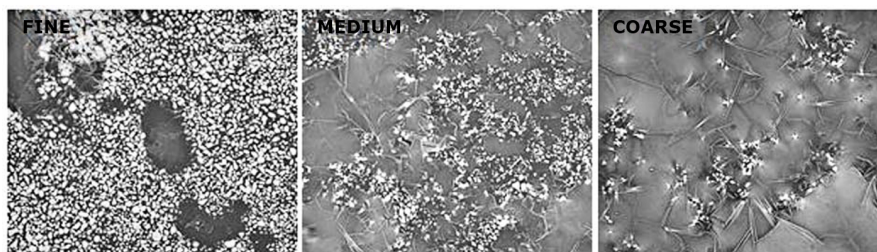


Figure 7. Surface appearance in the SEM at x3000 of the glazes at different glaze PSDs.

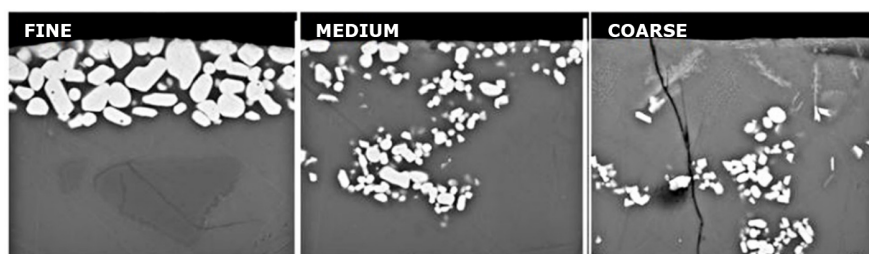


Figure 8. Cross-section in the SEM at x15000 of the glazes at different glaze PSDs.

5.2.3. EFFECT OF THE THERMAL CYCLE

Undoubtedly, as Rincón reported, the chemical reactions leading to dissolution largely depended on the thermal cycle used. The present study confirmed that lengthening the cycle or increasing peak firing temperature enhanced the crystallisations and, hence, the aesthetic properties of the resulting glaze.

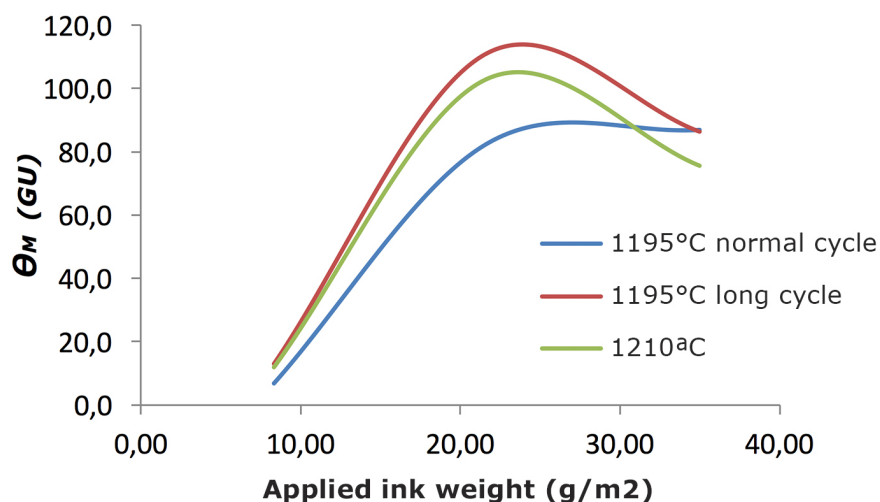


Figura 9. Correlación entre el brillo de vidriados sometidos a ciclos térmicos distintos según peso de tinta aplicada.

6. CONCLUSIONS

The present study was conducted as a result of the need to improve the efficiency of the development of the metallic effect resulting from the interaction of the ink with a glaze of appropriate composition, and the observation that similar crystallisations took place to those that developed when a single layer was applied. The study therefore pursued the optimisation of the most significant process variables. The study results confirmed the hypothesis that there was a stoichiometric ratio between phosphorus and iron in the surface, which optimised the development of the metallic effect on the piece. This required achieving control of the process parameters that influenced penetration of the coating and, therefore, of the chemical reactions that gave rise to the appearance of phase crystallisations that materialised in a strong metallic gloss.

The study showed that the quality of the metallic appearance depended on the ratio of the iron oxide and the phosphate concentration throughout the composition profile in accordance with the quantity of *inkjet* ink applied as a coating. It may be noted, with regard to the studied process factors, that the finer the particle size distribution of the glaze, the sooner did saturation occur owing to the glaze's low permeability. Moreover, an increase in firing cycle time and temperature improved nucleation and crystal growth in the glass matrix.

The study allowed greater control of the glaze-ink interface reaction to be achieved, enabling enhancement of the sought-after effect, as well as a better understanding of the type of crystallisations that develop, based on microstructural characterisation of the glazes.

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