DEVELOPMENT OF AESTHETIC EFFECTS THROUGH THE APPLICATION OF SUBMICRON MATERIALS

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1. ABSTRACT

The materials used for the decoration of ceramic tiles have evolved rapidly with the massive implementation of inkjet printing technology. The use of inks based on soluble complexes of transition metals has thus changed to the application of suspended solid particles (ceramic pigments) of sizes smaller than 1 µm. In these inks, the adjustment of different characteristics (viscosity and surface tension of the ink, particle size, etc.) has enabled products with good colour performance, stability and suitable behaviour in the print heads to be obtained.

At present, the application of the so-called effect inks (lustre, white, metallic, etc.) is being implemented using inkjet technology. In this case it is necessary to use frits and other raw materials, consequently introducing new requirements for inks apart from the traditional ones mentioned above. These requirements arise from the need to obtain thin continuous layers with the desired effect on the surface of the glaze, which must be integrated into the latter.

The objective of this study was to understand the most important requirements that effect inks must meet in order to establish the most appropriate procedures to obtain them.

It has been observed that the penetration of ink solids into the glaze, although improving integration, decreases the intensity of the sought effect and may disappear if penetration is excessive. This depends on the particle sizes of both the ink solids and the glaze, as well as on the type of solvent. On the other hand, it is important for the dimensional changes of the ink and glaze layers during heating and cooling to be similar, in order to prevent stresses from developing in the ink layer, which may crack it.

The work focused on inks in order to obtain two effects: the lustre effect and the floating white effect. The results have facilitated understanding of the key variables when preparing these effect inks, this being very important information in order to address the development of this type of product.

2. INTRODUCTION

The materials used for the decoration of ceramic tiles have evolved rapidly with the massive implementation of inkjet printing technology. The use of inks based on soluble complexes of transition metals has thus changed to the application of suspended solid particles (ceramic pigments) of sizes smaller than 1 µm. In these inks, the adjustment of different characteristics (viscosity and surface tension of the ink, particle size, etc.) has enabled products with a good colour performance, stability and suitable behaviour in the print heads to be obtained [[i], [ii], [iii]].

Currently, new inks are being developed that enable the use of inkjet technology to obtain certain aesthetic effects that were previously applied by rotogravure. These new inks, called "effect inks" enable development of different aesthetic effects (metallic, lustre, white, matte, "chameleon", etc.), and in many of them the use of frits and other raw materials is necessary, thus introducing new requirements.

Some of the problems that arise when using effect inks are related to the difficulty of obtaining thin continuous layers on the surface of the glaze into which they are integrated, which usually decreases or even in some cases eliminates the intensity of the desired effect. This may be due to multiple factors, among which is the degree of penetration of the ink into the glaze [[iv]], the mismatch of certain properties, such as thermal shrinkage or expansion, and the reaction mechanism causing the defect (devitrification, solid-gas reaction, etc.) [[v]].

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3. PROBLEMS ASSOCIATED WITH OBTAINING DECORATIVE EFFECTS USING SUBMICRON PARTICLE INKS

The development of submicron size inkjet inks, usually with a d_{99} <1 µm, entails a series of difficulties resulting from the small particle size of the applied materials. These problems are often related to the difficulty of obtaining thin continuous layers on the surface of the glaze into which they are integrated, which usually reduces or eliminates the intensity of the effect sought.

The small size of the ink solids (d_{99} <1 µm) allows the constituent particles to penetrate the glaze on which they are applied, usually with a much larger particle size (d_{99} = 45 µm) as indicated in the literature [4]. This penetration, although it favours integration of the ink into the glaze, may reduce the intensity of the desired effect on the surface when it is excessive due to loss of continuity of the applied layer.

In addition, the particle size distribution of the solids present in the ink is usually very narrow, notably worsening the packing of the applied layer. This increases shrinkage during firing and may cause cracks that deteriorate the aesthetic component [vi]. This same defect may also be caused by a mismatch in the coefficients of expansion, an important aspect to take into account when designing these materials.

Another aspect, also resulting from the small particle sizes in the inks, is the increased fusibility of the material, understood as a reduction in temperatures during transformation and softening. This intensifies the integration of the material applied on the glaze, although in extreme cases the desired defect may disappear. The opposite effect may also occur when the applied material is excessively refractory, as occurs when the ink has a high refractory raw materials content.

Finally, some mechanisms of effect formation are very sensitive to particle size, particularly those based on devitrification and solid-gas reactions [5, vii, viii]. In both cases, reduction in particle size may excessively increase the number of nuclei from which devitrification occurs, which negatively affects crystal growth and, therefore, the desired effect.

Some of these problems are discussed below, describing specific cases while providing possible solutions that may be implemented.

4. EXCESSIVE PENETRATION

Figure 1 shows the cross section of glazed pieces coated with white ink ground at different particle sizes (d_{99} = 45, 3 and 1 µm) observed by scanning electron microscopy (SEM). In the case of the ink with the largest particle size, application is via screen printing, while in the other two cases an inktester has been used. It is observed that in the ink applied using screen printing (top) the crystals and frit particles in the ink are in an area about 20 µm thick located at the surface of the glaze. In this area, the crystals are grouped in certain regions, which surround small areas without crystals that correspond to frit particles in the ink.

The ink with intermediate size particles (centre) has an appearance similar to that described above, forming a continuous layer about 20 µm thick in which both the crystals and frit particles of the ink are homogeneously distributed. The main difference with respect to the ink applied by screen printing is the smaller size of the crystal particles and frit particles.

As regards the pieces coated with the ink with the smallest particle size, it can be seen that the appearance of the layer is very different. There are bright regions formed by numerous very small crystals, as well as large areas free of crystals, thus yielding a layer with numerous discontinuities at the surface. The areas with crystals penetrate the glaze to a depth greater than 50 µm, and define areas without crystals that correspond to the glaze frit, to judge by the large size of these areas (> 20 µm). Surface discontinuity of the applied layer leads to a dull white effect due to excessive penetration of the ink into the glaze.

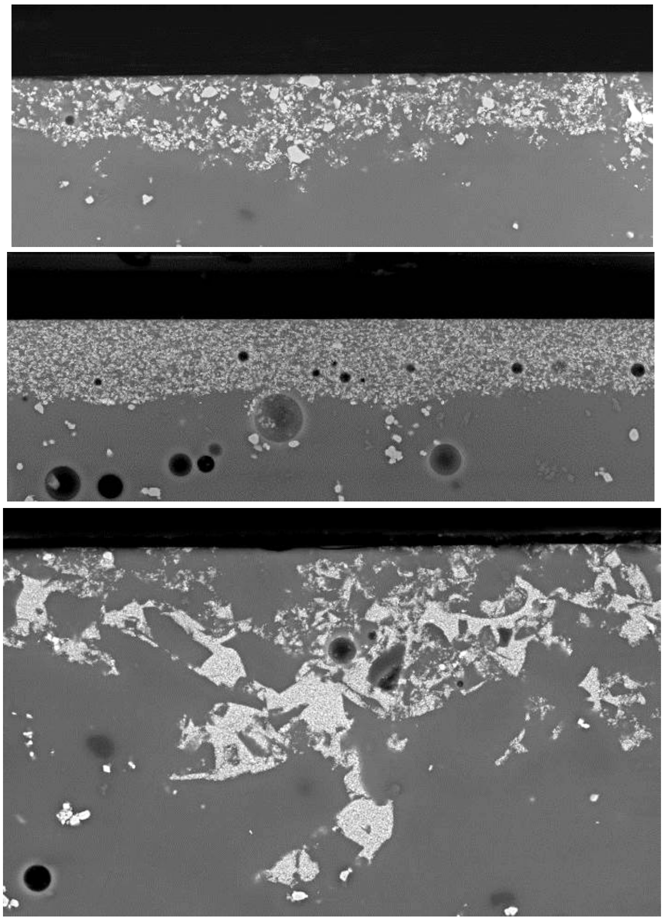

Figure 1. *Cross section of pieces coated with white ink with different particle sizes observed by SEM. Top: d99 = 45 µm, centre: d99 = 3 µm and bottom: d99 = 1 µm.*

Given that in the cross section of the piece with the smallest particle ink, it was observed that the ink solids had penetrated the glaze, the possibility was considered that penetration might have taken place either before or during firing. To see if there had been penetration in the unfired state, one of the unfired test pieces was observed using the backscattered electron signal of the SEM. This signal provides information about the topography and composition.

The images obtained are displayed in figure 2. In both pictures, the glaze layer is observed in the lower area of the images, which is formed by large grey particles between 10 and 50 µm, which are characterized by sharp angular edges. This, along with the EDX analysis carried out, indicates that these are frit particles. This layer also shows the presence of smaller laminar shaped grey particles, which correspond to the kaolin, and small bright particles (about 5 µm) with a rounder aspect, which correspond to the black pigment of the coloured transparent glaze. The upper part of the image displays a brighter layer formed by even smaller particles (<1 µm), which constitute the applied ink.

It is clearly observed that the material constituting the upper layer, of very small size, penetrates between the much larger frit particles (40 µm) to a depth, in some cases, of up to 50 µm, which indicates that a significant part of penetration occurs in the unfired state after application of the ink.

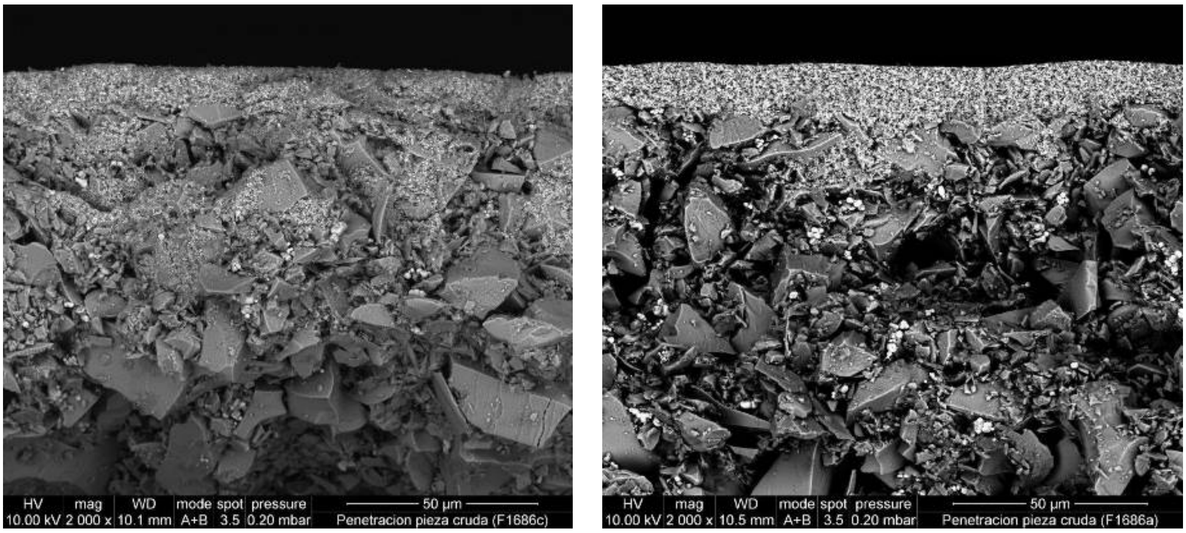

Figure 2. *Cross section of an unfired body coated with smallest particle ink (d_{99} = 1 µm), observed by SEM.*

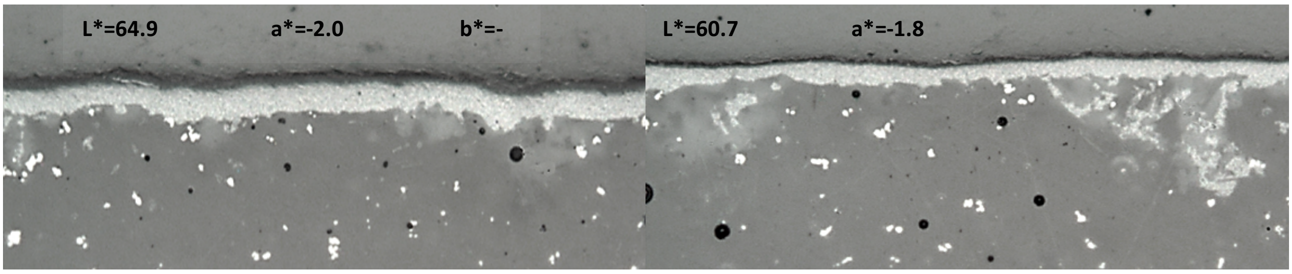

Figure 3. *Cross section of pieces coated with white ink observed by optical microscopy. Left: non-polar solvent, right: polar solvent.*

To understand the influence of solvent type on penetration in the unfired state, two zircon-based inks were prepared, one with a polar solvent and the other with a non-polar solvent. The inks, once prepared, have been applied to a transparent glaze coloured with black pigment and then fired, obtaining the chromatic coordinates displayed superimposed in figure **3.** The ink with non-polar solvent provides a higher value of the coordinate L* with respect to the ink with polar solvent, which is because it has penetrated less into the transparent glaze as seen in the aforementioned figure.

5. CRACKING OF LAYER

Figure 4 shows the appearance of the surface of pieces coated with a white ink of different particle size. In the images on the left of the figure, the ink was d_{99} = 45 µm and was applied by screen printing, while in those on the right, the ink was d_{99} = 1 µm and applied using inktester.

At low magnifications (100X, above), a large difference may be seen between the appearance of the parts coated with the two different inks. Thus, on the piece coated with the coarse particle ink, the presence of a continuous layer of brighter coloured crystals is observed in which some areas without crystals are present. In the samples coated with fine particle ink, cracks are observed in the coating, which break the continuity of the crystal layer.

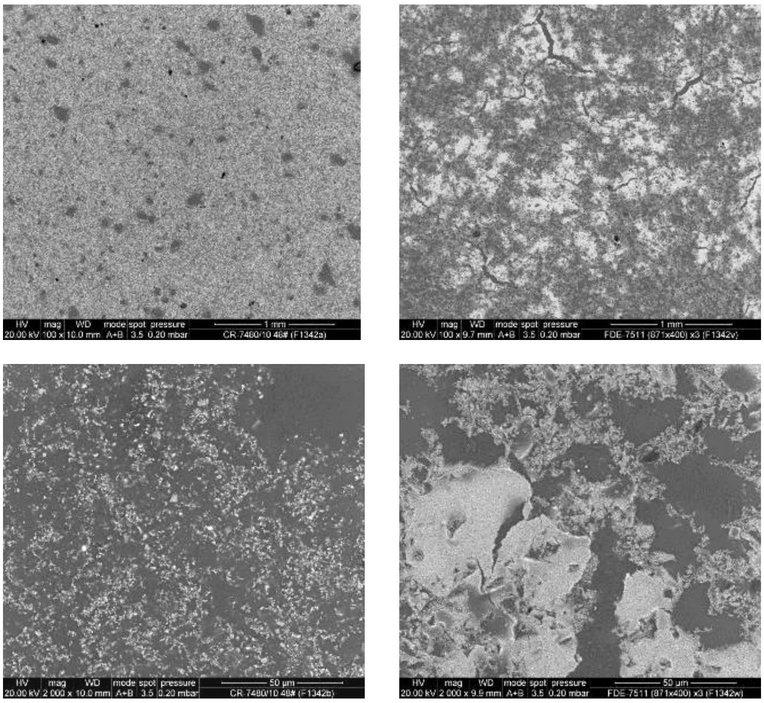

Figure 4. *Surface of pieces coated with white ink observed by SEM at different magnifications. Left: d99 = 45 µm, right: d99 = 1 µm.*

At higher magnifications (2000X, below), the crystals in the ink with larger particles begin to appear, which are distributed fairly homogeneously over the surface of the glaze. On the other hand, the pieces coated with the finer particle ink shows that the coating is completely cracked, with brighter coloured areas in which the crystals are still not distinguished due to their small size next to areas without crystals. These cracks are typical when applying coatings with a narrow particle size distribution and poor packing of the layer, causing cracks due to excessive shrinkage.

Another case of cracking of the coating may be observed in figure 5 where pieces coated with different white inks (C0, C1 and C2) are shown. For this type of defect to occur, there must be differing dimensional behaviour between the coating and the glaze on which it is applied, which occurs mainly during the firing stage, in both heating and cooling of the piece. Table 1 shows certain characteristics of the inks and glaze drawn from the hot stage microscopy test and the dilatometric curves.

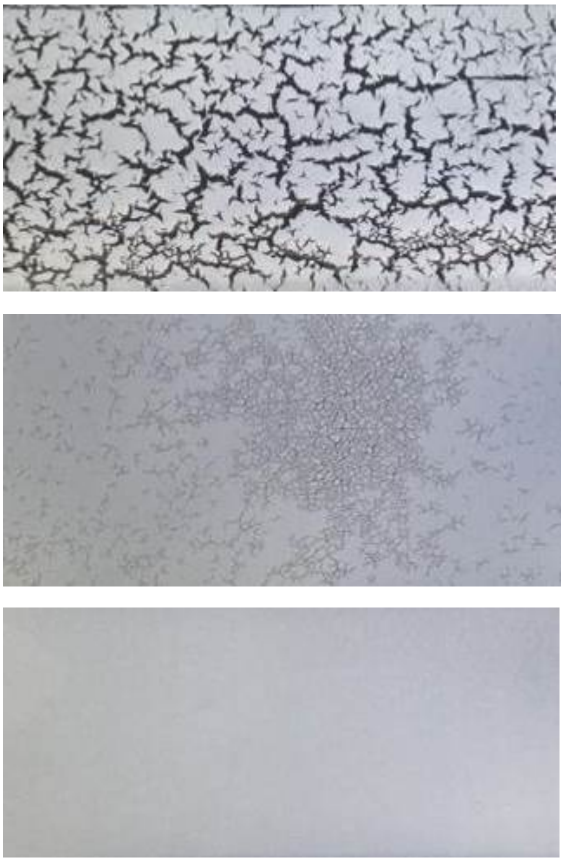

Figure 5. *Surface of pieces coated with different white inks observed by optical microscopy. Top: C1, centre: C2 and bottom C0.*

Characteristic	Glaze	C1	C2	C0
Shrinkage onset temp. (°C)	850	760	765	730
Shrinkage end temp. (°C)	1,010	1,150	960	935
Softening temp (°C)	1,055	1,165	1,255	1,060
Expansion at 700ºC (‰)	4.8	4.3	4.9	6.3
$\alpha_{50\text{-}300}$ (ºC^{-1}) x 10^7	61	67	65	78
$\alpha_{300\text{-}500}$ (ºC^{-1}) x 10^7	68	61	76	91

Table 1. *Characteristics of the glaze and white inks.*

The results obtained from the glaze-ink fit tests carried out using dilatometry measurements indicate that the cause of the cracks is not due to differing thermal shrinkage of the inks with respect to that of the glaze. It may therefore be concluded that in this case the cracks do not originate during cooling.

According to the results of the hot stage microscope, the three compositions could crack because they begin to contract prior to the glaze. To confirm this hypothesis, pieces were fired at different maximum temperatures in order to determine when cracking occurs. The appearance of the pieces is shown in figure 6. The following is observed:

- At 700°C, no cracks are observed in any of the inks, as shrinkage of the applied layers has not started.
- At 800°C, cracks are observed in inks C1 and C2, as shrinkage has started. Cracks were also observed on opening the kiln at 800°C in order to avoid the influence of cooling.
- Starting at 800°C, the cracks in inks C1 and C2 grow as a result of shrinkage of the applied layer.

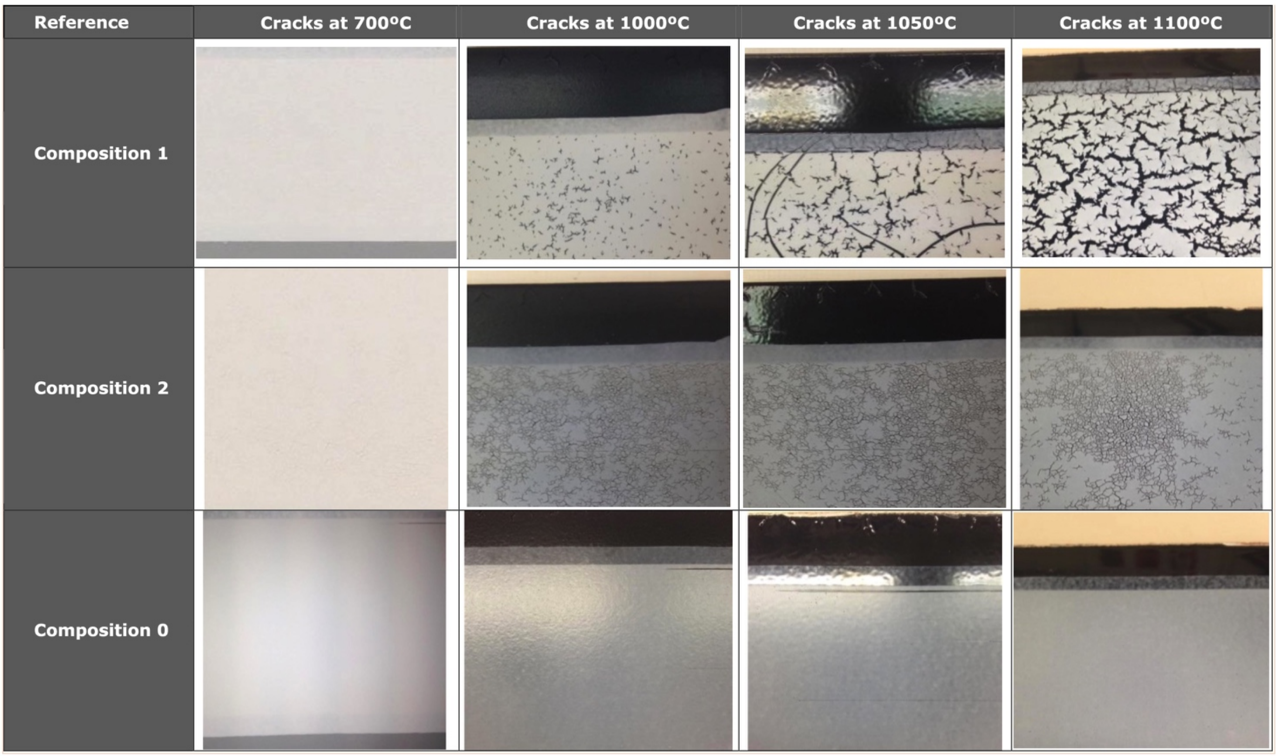

Figure 6. *Surface of the pieces coated with different white inks and fired at various maximum temperatures.*

6. AREAS WITH NO EFFECT

When it comes to using inkjet printing to reproduce an effect traditionally obtained using screen printing or rotogravure, the first step is to reduce the particle size of the traditional ink to the size required by inkjet technology. Unfortunately, on many occasions the desired effect is eliminated on reducing the particle size of the ink. An example of this case is observed in figure 7, in which surface and cross-sectional images of a lustre effect achieved using frit that devitrifies a solid solution of ZrO_2 in CeO_2 (hereinafter referred to as CeO_2 for simplicity) are shown.

Most of the surface of the piece with ink ground at 45 μm has a whitish hue (top-left) due to the CeO_2 crystallites, which cover it and can be seen in more detail in the centre image (Figure 7); these crystals have been formed from the frit by devitrification.

The bottom left image (Figure 7) shows a cross section of the piece displaying the small CeO_2 crystals observed at the surface. These crystals form a continuous layer at the surface of the piece. Below this surface layer is a strip of glass without crystals about 400 nm thick. When this area of glass ends, these crystals are again arranged randomly, although in some cases it would seem that they define the edges of what were initially frit particles (what might have been one of the frit particles has been drawn in red). For the larger cerium oxide crystals, their cubic shape is clearly visible. Finally, in addition to these crystals, there are some much larger needle-shaped crystals, of zircon. The results obtained indicate that the lustre effect is due to the thin layer of CeO_2 crystals covering the surface of the piece, forming a continuous layer.

In the images on the right (Figure 7 top and centre) the appearance of the surface of the pieces coated with ink ground at d_{99} = 3 μm is shown, these pieces not displaying the lustre effect. It is observed that the CeO_2 crystals at the surface are much less numerous while bordering some cells whose interior is glassy and, in many cases, has a centre pore (black).

The image in figure 7 at the bottom right shows the cross section of the piece on which it may be seen that the devitrified crystals form agglomerations and do not form a continuous layer at the surface on the piece. The absence of a continuous coating of crystals with high refractive indices at the surface of the piece explains why the ink ground at 3 μm does not provide a lustre effect.

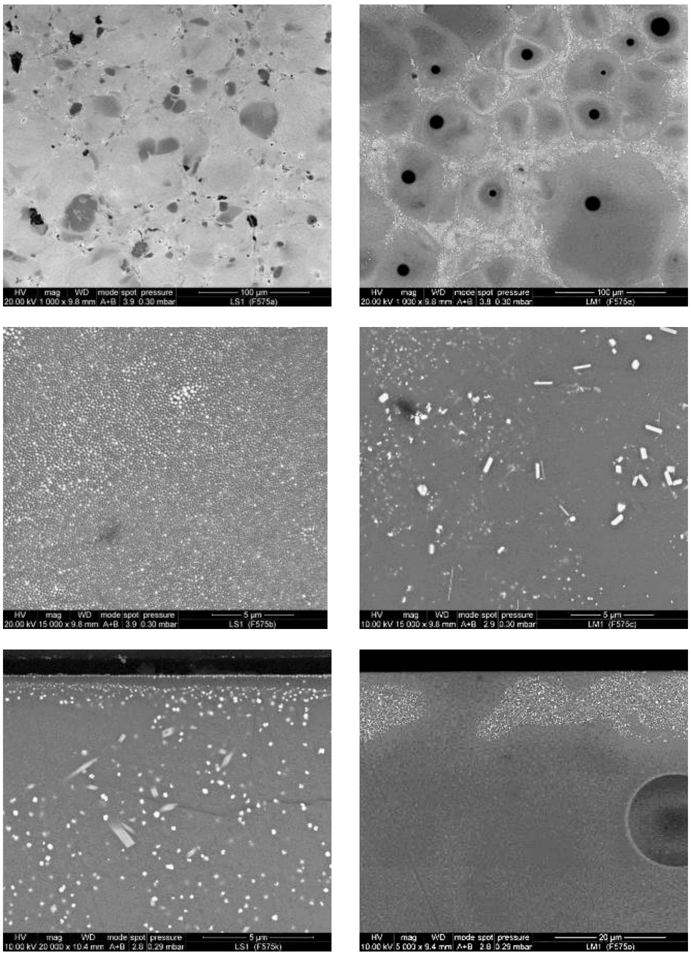

Figure 7. *Surface (top and centre) and cross section (bottom) of pieces coated with lustre ink observed by SEM. Left: d99=45 μm, right: d99=3 μm.*

In order to determine why the surface of the pieces with lustre ink ground at 3 μm had no lustre effect, the pieces were fired at different maximum temperatures (1040, 1120 and 1135°C), as shown in figure 8. It is observed that at 1040°C there is a layer of whitish crystals that covers the piece in which some dark areas corresponding to the glaze are visible. On increasing the firing temperature (1120 and 1135°C) the number of dark areas without crystals increases, forming the cells observed in the pieces of figure 7. The bottom-right image shows an enlarged view of the surface of the piece at 1135°C, in which there are groups of crystals, which are actually small particles from the frit in the ink. These groups are separated by small breaks, indicating that the crystals are moving and reorganizing.

In order to determine the causes of this movement of crystallites (or frit particles), cross sections of the fired pieces have been observed at various maximum temperatures (Figure 9). In these, it may be observed that at 900ºC the ink layer has already melted, while the glaze has a porous texture indicating that the fusion process has not yet begun. It is also observed that the ink layer is penetrating and diffusing inwards, at higher temperatures causing frit particles from the base glaze to surface, creating the cells in figure 7, which grow with the increased temperature.

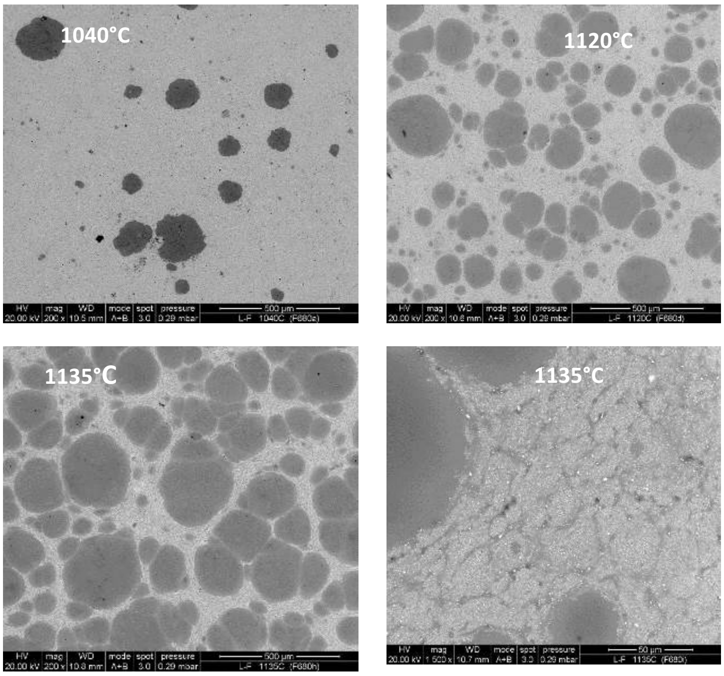

Figure 8. *Surface of pieces coated with lustre ink (d99 = 3 µm) fired at different maximum temperatures observed by SEM.*

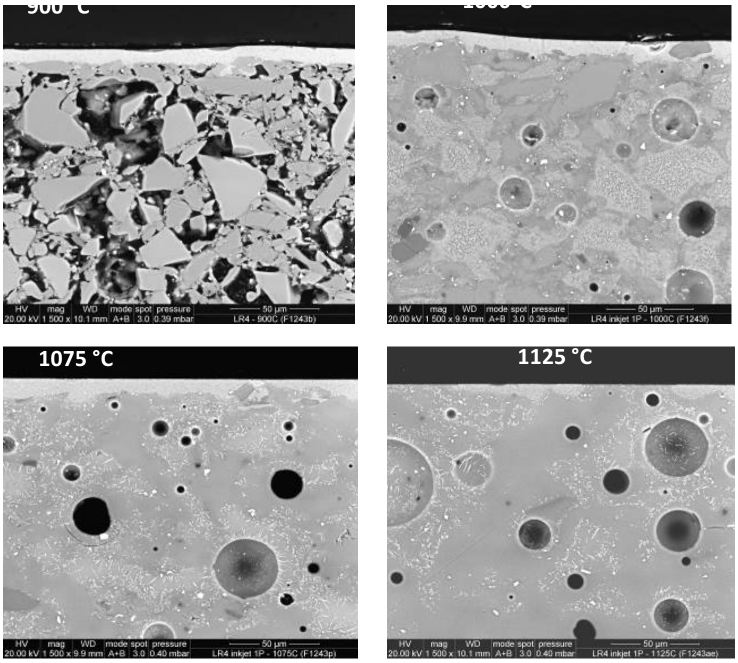

***Figure 9**. Cross section of pieces coated with lustre ink (d99 = 3 µm) fired at different maximum temperatures observed by SEM.*

7. REDUCTION OF EFFECT INTENSITY

Sometimes, the materials developed to obtain the inks provide a lower intensity of the effect when applied by inkjet. An example of this behaviour may be observed in inks containing, as a main element, a frit that devitrifies CeO_2. Figure 10 shows, for comparison, the surface of pieces coated with coarse particle (d_{99} = 45 µm) and fine particle (d_{99} = 3 µm) lustre inks. It is observed that in the coarse particle ink the crystals are oriented, have a more uniform size and are larger (80-140 nm) than those in the fine particle ink (50-115 nm). It may also be seen that the crystals in the coarse particle ink have sharper edges than those in the fine particle ink, whose edges are, in many cases, diffuse. This is because in this last image some of the crystals observed lie deeper and not at the surface.

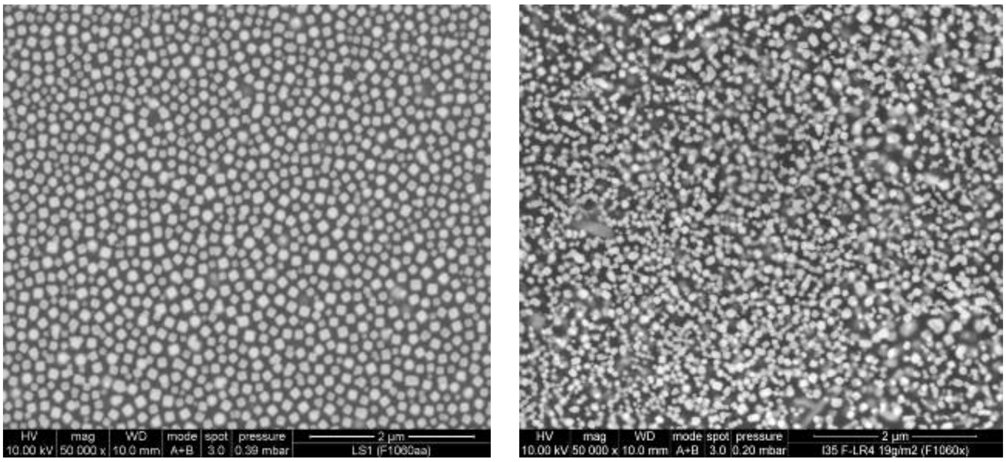

Figure 10. *Surface of pieces coated with lustre ink, observed by SEM. Left: d99=45 µm, right: d99=3 µm.*

Figure 11 shows a diagram of the devitrification of CeO_2 crystals, in black, from a frit, in grey, with large and small particle sizes. As devitrification takes place preferentially at the surface of the frit particles and the signal from up to 3 µm depth ("d" in the image) reaches the SEM detector, at the surface obtained with the less ground ink (left) only the crystals located at the surface of the piece are detected. On the other hand, for the more ground ink (right), the signal that reaches the microscope detector comes from both the crystals at the surface and those at a certain depth (sub-surface), as shown in the scheme in figure 11.

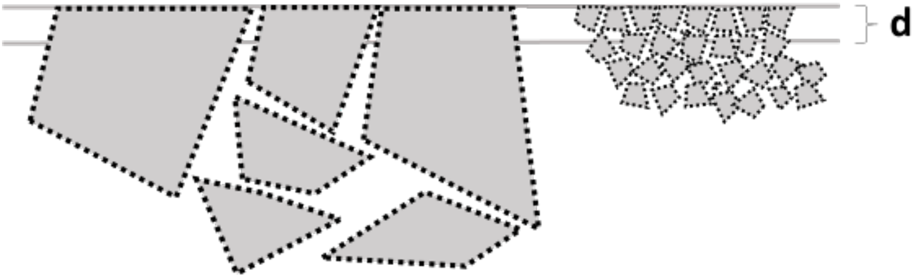

Figure 11. *Scheme of the cross section of a piece with frit particles that devitrify CeO_2. Left: d_{99}=45 µm, right: d_{99}=3 µm.*

This devitrification mechanism has been described by other researchers [ix-x], who have observed that, in silicate glasses, nucleation occurs at the surface of particles, especially at edges and boundaries created by fracture (grinding). Other studies [xi] conclude that coalescence, during thermal treatment, of glass particles prior to crystallization produces a reduction of the surface area, however leaving, even after coalescence, traces (memory) of the original surfaces as areas where crystallization starts.

The foregoing demonstrates the importance of particle size on devitrification, since the crystals will form at the surface of what were initially glassy particles and, consequently, frit particle size will affect the number of crystals formed and possibly their size. Thus, in inks with small frit particles a greater number of nuclei may form with respect to inks with large frit particles; however, for all these nuclei to grow, a greater amount of reagent will be required.

8. CONCLUSIONS

This study addresses certain aspects to consider when formulating inkjet effect inks, based on white inks with lustre effect. It has been found that penetration of the solids contained in the ink into the glaze affects the intensity of the desired effect and depends to a large extent on the particle size and solvent used. Thus, inks with d_{99} = 1 µm show a certain tendency to penetrate in the unfired state, whereas when size increases to d_{99} = 3 µm, penetration is minimal, especially when using non-polar solvents. As regards cracking of the ink layer, this may occur both during the heating and firing phase, as well as during cooling, due to a significant difference in thermal expansion between the ink and glaze layers. The greater dimensional variation that these materials undergo during the heating and firing phase, with respect to the cooling phase, results in the former being the primary cause of cracking, which can be corrected by regulating the fusibility of the applied ink. Excessive ink fusibility also leads to areas with no effect, as early melting of the ink enhances ink penetration between the frit particles of the glaze that have not yet melted, which makes them surface, eliminating the desired effect. Finally, the effects achieved by crystal devitrification from the ink frit particles are greatly influenced by particle size. Therefore, although decreased particle size increases the number of nuclei formed, growth is compromised by the need for greater amounts of crystal-forming elements, which may decrease the amount of devitrified crystals at the surface and their size, thus decreasing the intensity of the effect.

9. REFERENCES

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