LUSTRE EFFECT: MECHANISM AND INFLUENCE OF PARTICLE SIZE

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1. ABSTRACT

The “lustre” effect consists of a high gloss of the fired glaze surface, with tones that change depending on the impinging light, giving the piece a pearly appearance. This occurs when the light crosses a thin film on the glaze surface, whose refractive index is much higher than that of the glaze on which it is deposited. This surface film can be obtained by different methods: reaction between the frit in the base glaze and a material applied on the surface of the unfired glaze, devitrification from a frit, or vapour phase deposition (CVD or PVD) on a fired glazed piece. The so-called “tungsten lustres” are obtained by the first method. A thin film of scheelite crystals forms, whose refractive index is 1.92–1.93 as opposed to that of silica glasses, which is of the order of 1.5, by reaction between the tungsten applied on an unfired glaze, in the form of an oxide or a metal, with the calcium in the glaze composition.

It was verified that the effect was obtained when scheelite ($CaWO_4$) formed in situ during the firing of the piece, giving rise to oriented crystals, and that the application of the $CaWO_4$ precursors on the unfired glaze generated a refractory surface without any type of effect, probably owing to the random orientation of the applied crystals.

The reaction between W and Ca took place at the surface of the frit particles and frit particle size considerably affected the result. When the frit had a large particle size (d_{90}=40 µm), typical of bell glazing applications, the reaction surface was not very great and allowed a surface film of $CaWO_4$ to form that produced the effect. In contrast, when the frit particles were small (d_{90}=3 µm), the reaction surface with W increased and a $CaWO_4$ crystal skeleton formed that surrounded the frit particles, coating them and generating a rigid structure ($CaWO_4$ crystals are very refractory), which prevented viscous flow sintering and did not form the necessary surface film to produce the sought-after decorative effect.

2. INTRODUCTION

The “lustre” effect, also known as “nacre”, “mother-of-pearl”, or “iridescence”, develops as a result of the interference of light when it crosses a thin surface film whose refractive index differs from that of the base on which this layer is placed, the light being partly reflected (like an oil film on water). In ceramic glazes [1] this effect is obtained with a layer of crystals that have a high refractive index, as the refractive index of a silica glass is low (about 1.5–1.6).

The word lustre comes from the Latin word lux, which means gloss. Lustre can be metallic [2] when it is opaque and highly reflective, as in metals. It can be pearly, when layers with very different refractive indices are superimposed on each other, and it can be iridescent when it changes colour as a function of the angle of observation. These changes are sometimes interference colours between layers 20 to 200 nm thick.

In the literature, the term lustre has been used for glazes with a metallic appearance, produced between the 9th and 12th centuries in the Middle East, Spain, and Italy [3], this being defined as a thin film of metal–glass nanocomposite [4] with singular optical properties, exhibiting iridescences and changes in colour as a function of the size of the nanoparticles scattered in the glass [5]. Some studies [6] refer to lustres as the predecessors of glazes with a metallic gloss, indicating that they were obtained using metals such as copper, iron, tungsten, silver, and sometimes gold. These authors differentiate between lustre glazes and metallic glazes, noting that the latter are obtained by a different method, in which metals are added in powder form to the glaze composition.

In any event, the high gloss characteristic of the lustre effect stems from a surface layer that can be obtained by different mechanisms: reaction between the frit in the base glaze and a material applied on the surface of the unfired glaze [1] [2], devitrification from a frit [7] - [8], metal particle precipitation on the glaze surface [9], or vapour phase deposition (CVD or PVD) on a fired glazed piece. This last method, as a function of the material and thickness of the deposited layer, yields glazes with a metallic appearance.

The most widely used lustres at present in ceramic tile manufacture are based on scheelite ($CaWO_4$) [1] - [2] and on cerium oxide [7] - [8]. In the former, during tile firing, an oriented layer of scheelite crystals forms by reaction between a frit and W, applied as an oxide or a metal. Cerium lustres are a more recent development and they develop by devitrification of a thin film of oriented crystals of cerium oxide [8] or of cerium oxide and zirconium [7].

Regardless of whether the thin film of crystals with a high refractive index on the glaze is produced by reaction or devitrification, frit particle size must affect the resulting microstructure [10] and, consequently, the intensity of the effect. This study examines the influence of the size of the frit particles that react with W to produce scheelite on the intensity of the resulting lustre effect, as well as the formation mechanism of this effect.

3. EXPERIMENTAL

3.1. MATERIALS

The study was conducted using a frit that gives rise to transparent glossy glazes (frit C), customarily used in porcelain tile manufacture, and a commercial tungsten oxide from Alfa Aesar, with an average particle size of 2 μm. The chemical composition of the frit is detailed in Table 1.

SiO_2	Al_2O_3	Na_2O	K_2O	CaO	B_2O_3	ZnO
70	8	2	6	12	1	1

Table 1. *Chemical composition of the frit used.*

3.2. EXPERIMENTAL PROCEDURE

The frit was applied on an unfired porcelain tile body. The pieces were then dried, followed by firing at 1180 °C in an electric laboratory kiln. Gloss was measured on the fired pieces and they were observed by scanning electron microscopy.

The frit was milled to two particle sizes, obtaining d_{90} values of about 40 and 3 μm. Milling to 40 μm was performed in planetary ball mill, while a bead mill was used to obtain 3 μm. A tungsten oxide (WO_3) suspension was prepared in water with a solids content of 40% using carboxymethylcellulose as a binder.

The frit suspensions were applied by spraying at right angles to the previously moistened body. The applied quantity was 20 g/m^2. The glazed test pieces were then dried at 110 ºC in an electric laboratory oven, with air recirculation. After the glaze had been dried, a very small quantity (about 2 g/cm^2) of the tungsten oxide suspension was applied and the test pieces were dried again.

The test pieces were fired in an electric laboratory kiln to a peak temperature of 1180 °C at a heating rate of 25 ºC/min. Residence time at peak temperature was 6 minutes and cooling was performed by forced convection. Firings were also carried out at 25 ºC/min to peak temperatures of 800, 900, and 1000 ºC.

The polished cross-section and surface of the pieces were observed with the backscattered electron signal of a field-emission gun environmental scanning electron microscope FEG-ESEM FEI Quanta 200.

4. RESULTS

4.1. INFLUENCES OF FRIT PARTICLE SIZE

Visual observation of the test pieces fired at 1180 °C showed that the glaze resulting from the WO_3 application of the frit milled at 40 μm (C/40) exhibited a lustre effect, whereas when the WO_3 had been applied on the same frit with a fine particle size (C/3), there was no lustre effect. It was further noted that the surface texture of the piece with the lustre effect (C/40) was smooth, whereas that of the pieces obtained using the frit milled in the bead mill was very rough, suggesting that a very refractory phase had formed that prevented glaze stretching. On the other hand, the surface of a piece obtained by applying frit C/3, without spraying WO_3, was also smooth and glossy.

Figure 1 depicts images, at two magnifications, of the glazed surface of the three pieces obtained with frit C. Frit C/3, without applying WO_3, (Figure 1a and 1b) provided a very smooth glaze, mainly consisting of glassy phase, in which some crystals could be distinguished, whose analysis indicated a higher calcium content than the matrix. The surface of the fired glaze obtained with frit C/40 displayed the same appearance as that obtained with frit C/3.

The glaze obtained on spraying WO_3 on frit C/40 (Figure 1c and 1d) displayed a much smoother surface than that obtained with frit C/3 (cf. Figures 1c and 1e). Both glazes exhibited glossy, small-sized crystals that totally covered the surface of piece C/40 (Figure 1d), whereas they were much more scattered at the surface of C/3 (Figure 1f). Analysis of these crystals showed a high proportion of W and Ca, so that $CaWO_4$ must be involved, formed by reaction of W with Ca in the frit.

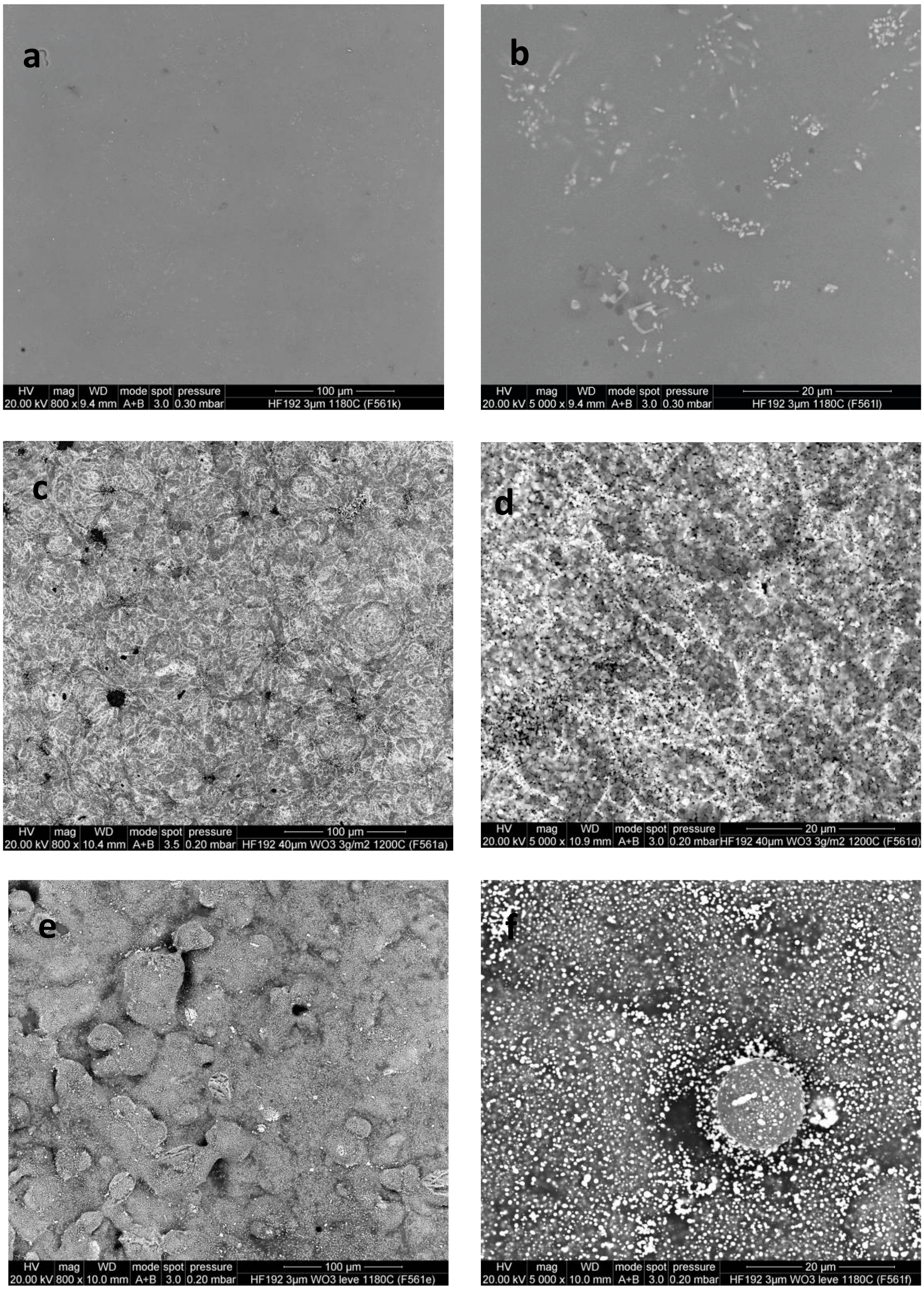

Figure 1. *Surface appearance of the fired glazes at x800 (left) and x5000 (right) magnifications. Frit C/3 without* WO_3 *(a, b), frit C/40 with* WO_3 *(c, d), and frit C/3 with* WO_3 *(e, f).*

Figure 2 shows in greater detail that the glaze C/40 surface was completely covered with crystals, whereas in the glaze C/3 surface (Figure 2b) the crystals were widely scattered in a glass matrix. These differences in $CaWO_4$ crystal density in the glaze surfaces led the piece with C/40 to display a lustre effect, which the piece with C/3 did not. However, the differences in surface roughness of the two glazes remained unexplained (Figure 1c and 1e), which is why cross-sections of the pieces were observed.

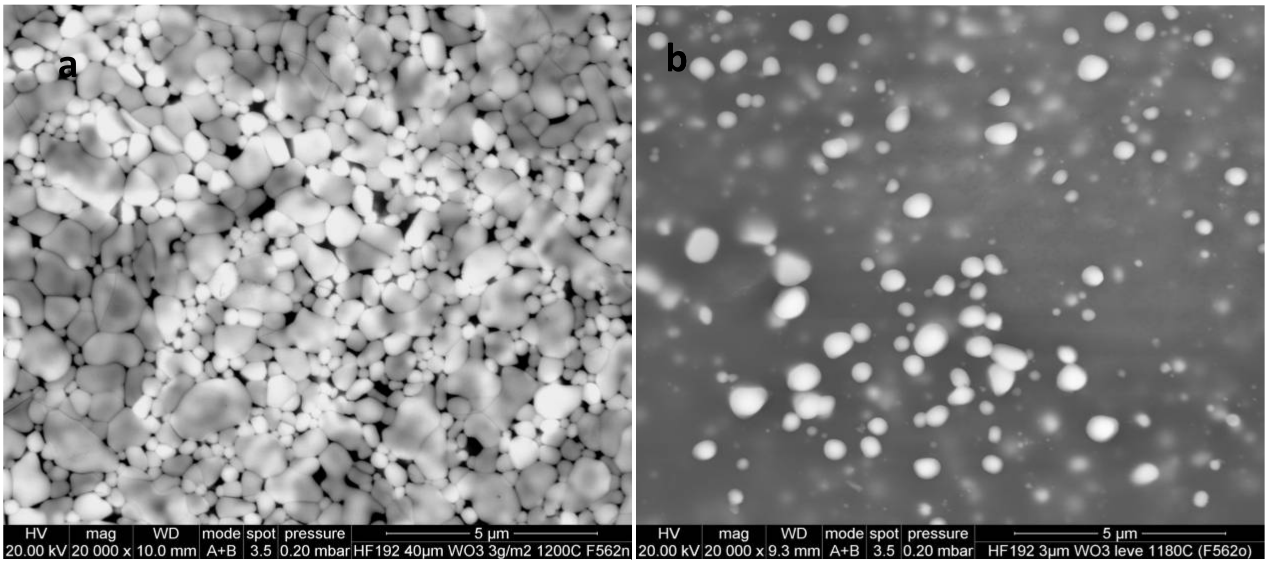

Figure 2. *Surface of fired glazes C/40 (a) and C/3 (b) with the WO_3 application.*

At low magnification, the cross-section of the fired glaze with C/40 (Figure 3a) displayed a series of gentle undulations in the glaze surface, whose heights exhibited a separation of 200–300 µm. In contrast, in the piece with C/3 (Figure 3b), protuberances with sharper edges were observed with spacings between them of about 100 µm. The profile of this piece was similar to that which would have been obtained if particles of a refractory material had been applied (e.g. coarse corundum), which had remained stuck to the piece and had then been partially softened during firing, without integrating in the melt.

At greater magnification, glaze C/40 (Figure 3c) displayed a continuous white film of $CaWO_4$ particles in the surface of the piece while, towards the inner part of the glaze, $CaWO_4$ crystals were heterogeneously distributed, forming clusters or veins. In contrast, the cross-section of piece C/3 (Figure 3d) revealed that the $CaWO_4$ crystals were homogeneously distributed throughout the thickness of the glaze and did not form clusters. The different distribution of the $CaWO_4$ crystals may be observed in greater detail in Figure 4. The $CaWO_4$ clusters in Figure 4a can be clearly seen in the surface of the piece, surrounding what might initially have been frit particles. In Figure 4b the crystals were individualised and homogeneously distributed throughout the volume of the glaze, without forming a continuous layer at the surface.

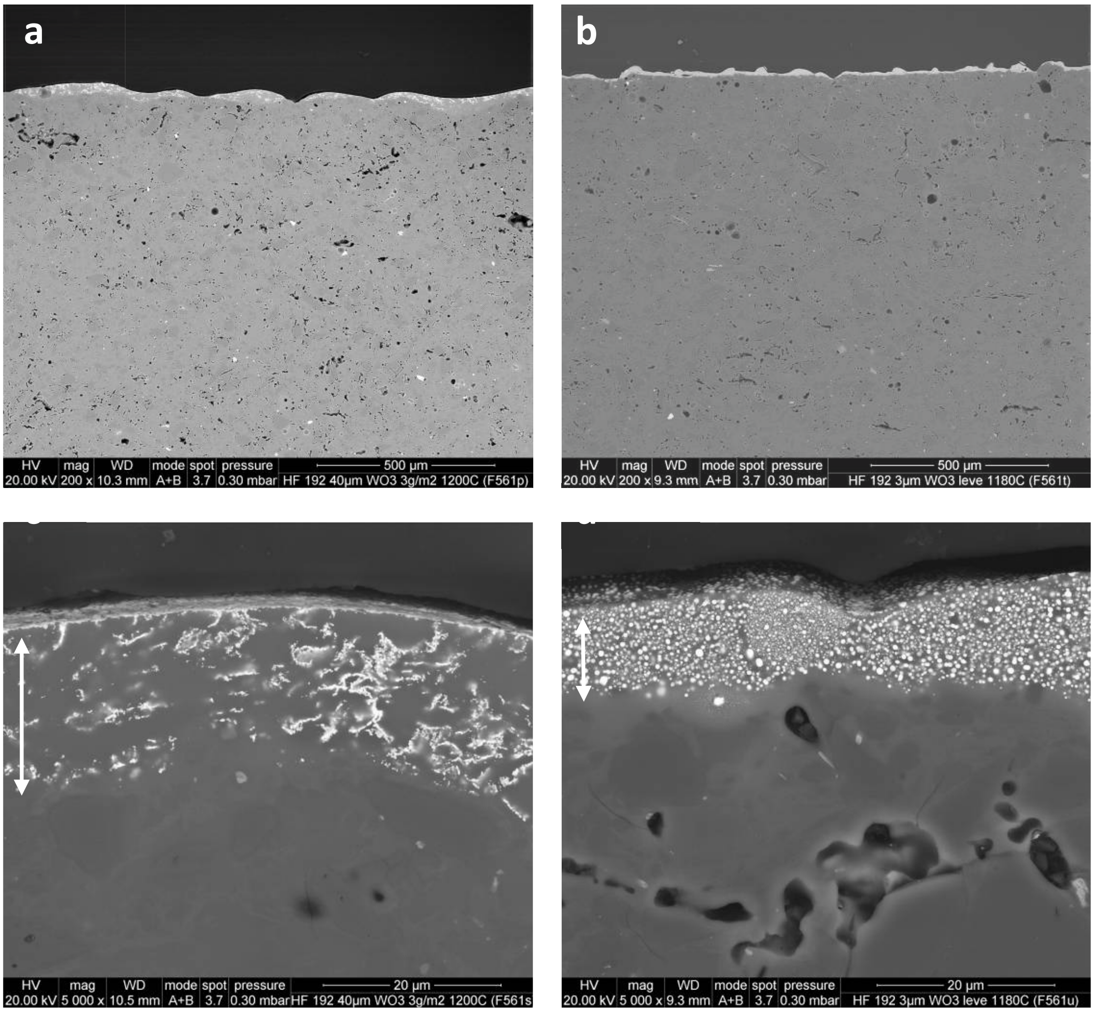

Figure 3. *Cross-section of the fired glazes obtained with frit C at x200 (top) and x5000 (bottom). Frit C/40 (a, c) and C/3 (b, d).*

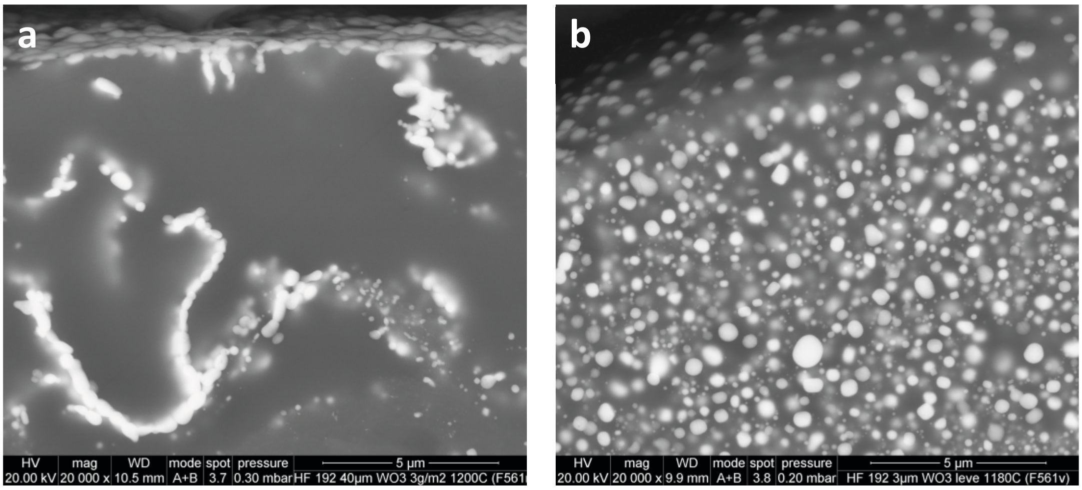

Figure 4. *Cross-section of the fired glazes obtained with frit C. Frit C/40 (a) and C/3 (b).*

Figure 5 shows the polished cross-section of the C/3 piece observed by SEM at low voltage (10 kV). The electron acceleration voltage affects the interaction volume with the sample, which decreases as voltage decreases (greater surface signal). It may be observed that between the $CaWO_4$ particles there were glass zones (some have been marked in red in the figure) that, owing to their size, must correspond to what were initially frit particles. These results indicate that the reaction between WO_3 applied to the Ca in the frit to yield $CaWO_4$ took place at the surface of the frit particles, though it is still not known why, when the frit was fine, the surface of the piece was not entirely covered with $CaWO_4$.

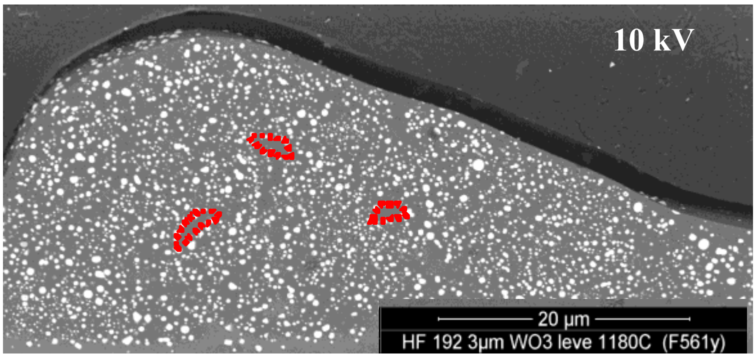

Figure 5. *Cross-section of the fired glaze obtained with frit C/3 at 10 kV.*

4.2. CAWO$_4$ FORMATION IN THE FIRED GLAZE SURFACE

In order to attempt to get the $CaWO_4$ crystals that formed during firing to position themselves preferentially at the surface of the glaze, tests were performed applying three layers on the porcelain tile body. The coating was obtained by applying, first, a suspension of the C/3 frit, secondly, a suspension of kaolin to avoid contact of the WO_3 application with the frit and, finally, a suspension that contained a mixture of WO_3 and $Ca(OH)_2$ in a stoichiometric proportion to form $CaWO_4$. The objective was to get the reaction between the W and Ca to take place at the surface, between the constituents of the last applied mixture.

Figure 6 shows the surface appearance of the piece. It may be observed that the mixture of WO_3 and $Ca(OH)_2$ reacted to produce the targeted $CaWO_4$ crystals, though these were neither oriented nor embedded in the glass matrix but formed agglomerates, so that they did not provide the sought-after lustre effect. Cross-sections of the samples (Figure 7) confirmed that this technique did not provide a continuous layer of $CaWO_4$ crystals embedded in the fired glaze.

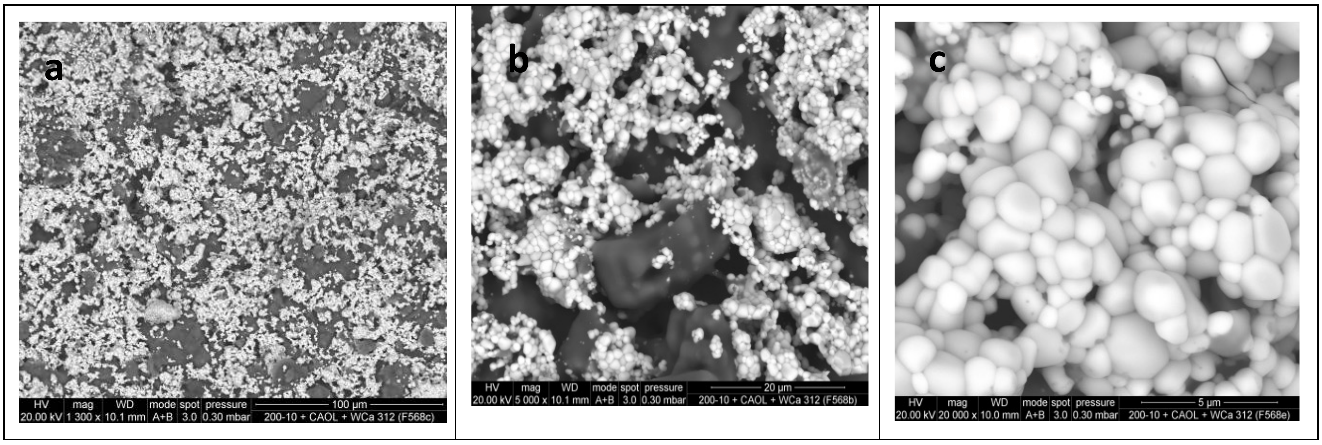

Figure 6. *Appearance of the three-layer coating surface: (a) x1300; (b) x5000; and (c) x20000.*

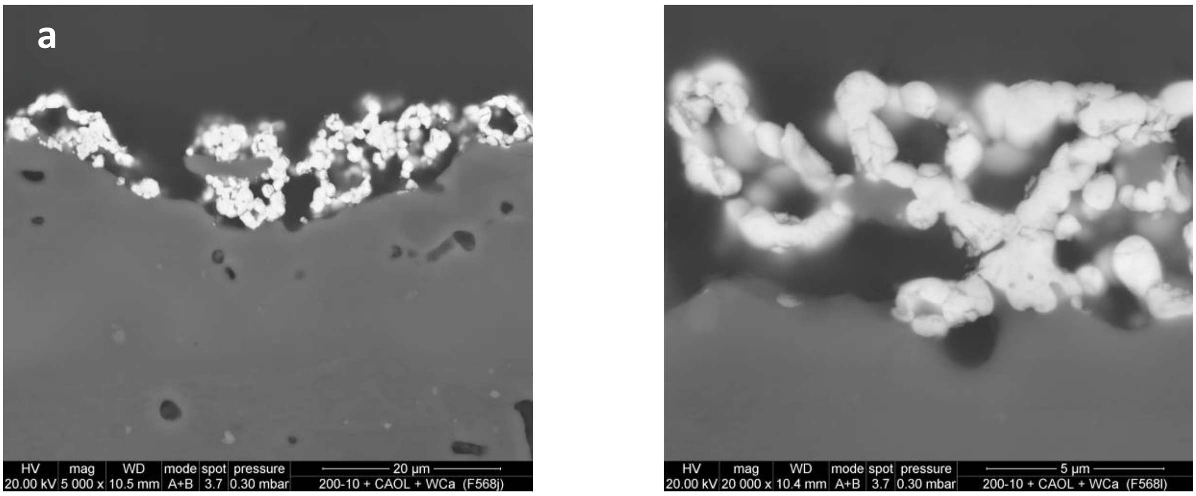

Figure 7. *Appearance of the cross-section of the three-layer coating: (a) x5000; and (b) x20000.*

4.3. EVOLUTION OF MICROSTRUCTURE WITH FIRING TEMPERATURE

In order to attempt to understand why the lustre effect was not obtained when WO_3 was sprayed on a layer of finely milled frit, it was decided to observe the evolution of the microstructure of the pieces with firing temperature. To do so, a layer of C/3 frit was applied on an unfired porcelain tile test piece and the tungsten suspension was applied on this layer. The pieces were fired at different maximum temperatures: 800, 900, and 1000 °C. Figure 8 shows polished cross-sections of these pieces, at different magnifications.

These images show that $CaWO_4$ only formed in the top zone of the thickness of the applied frit layer. The $CaWO_4$ that had formed surrounded the frit particles perfectly, making these look "coated in batter". As $CaWO_4$ is very refractory, when it surrounded the frit particles, which were such a small size, it prevented them from softening and producing a smooth fired glaze at the porcelain tile firing temperature, which explains the surface texture observed in Figure 3b. In the bottom zone of the frit layer, where there was no reaction, the frit particles softened, sintered, and formed a compact layer as the temperature rose.

The arrangement of the $CaWO_4$ crystals was not explained by penetration of the sprayed WO_3 into the unfired frit particle layer, as in this case it would not have been so homogeneous. In addition, the applied WO_3 had a particle size similar to that of the milled frit, which prevented its penetration.

Based on the results obtained, it was decided to observe the microstructure of the unfired and fired test piece surfaces at 800, 900, and 1000°C. This yielded the images shown in Figure 9. It may be observed that the applied WO_3 particle size (Figure 9a) was much larger than that of the arising $CaWO_4$ (Figures 9b to 9d) and that the change in microstructure from the unfired to the fired piece could only be explained by a vapour-phase mechanism. On consulting the literature [11]-[12], it was verified that WO_3 sublimation began at 750°C, which allowed this oxide to diffuse in the vapour phase during preheating in the kiln inwards into the frit layer and to react with the calcium in the frit to form the $CaWO_3$ crystals that coated the frit particle surfaces.

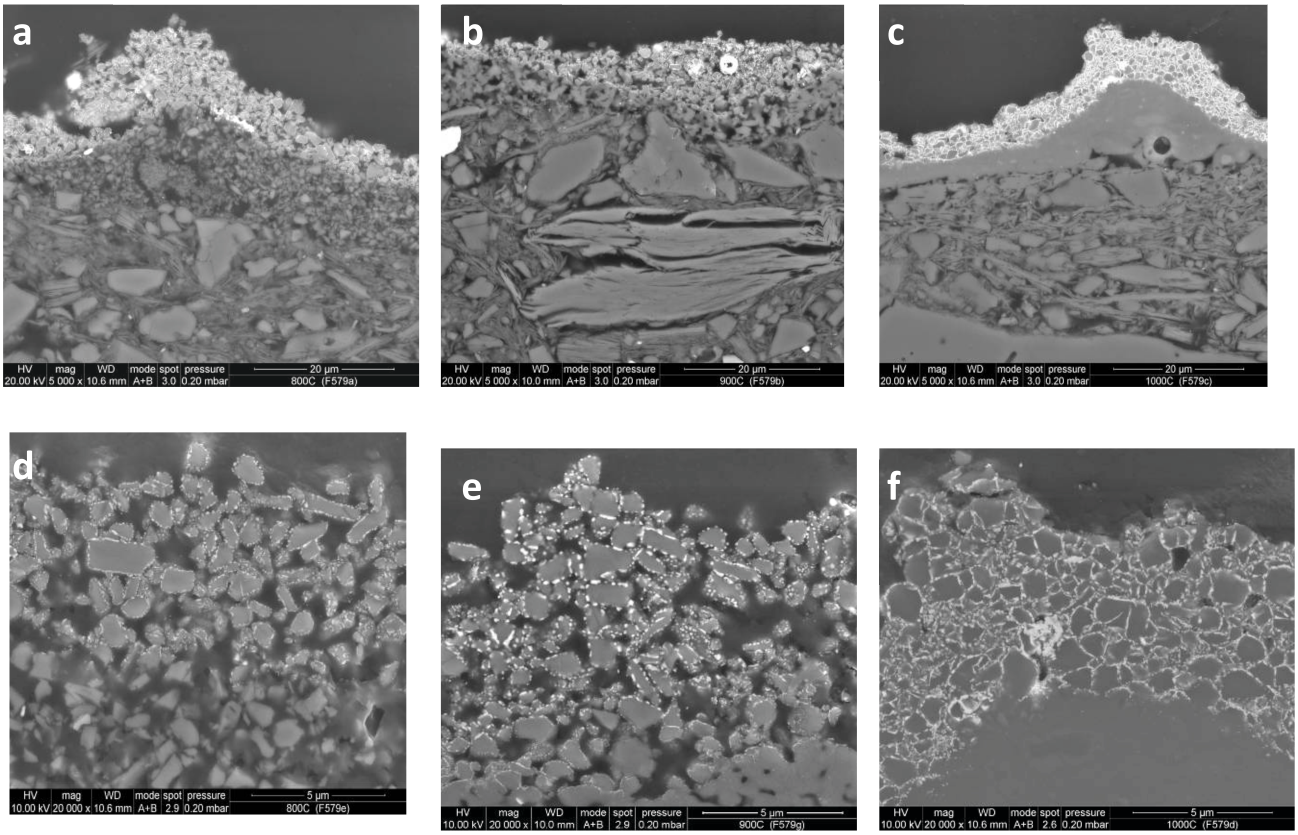

Figure 8. *Cross-section of the coating at x5000 (top) and x20000 (bottom). 800 °C (a, d), 900°C (b, e), and 1000 °C (c, f).*

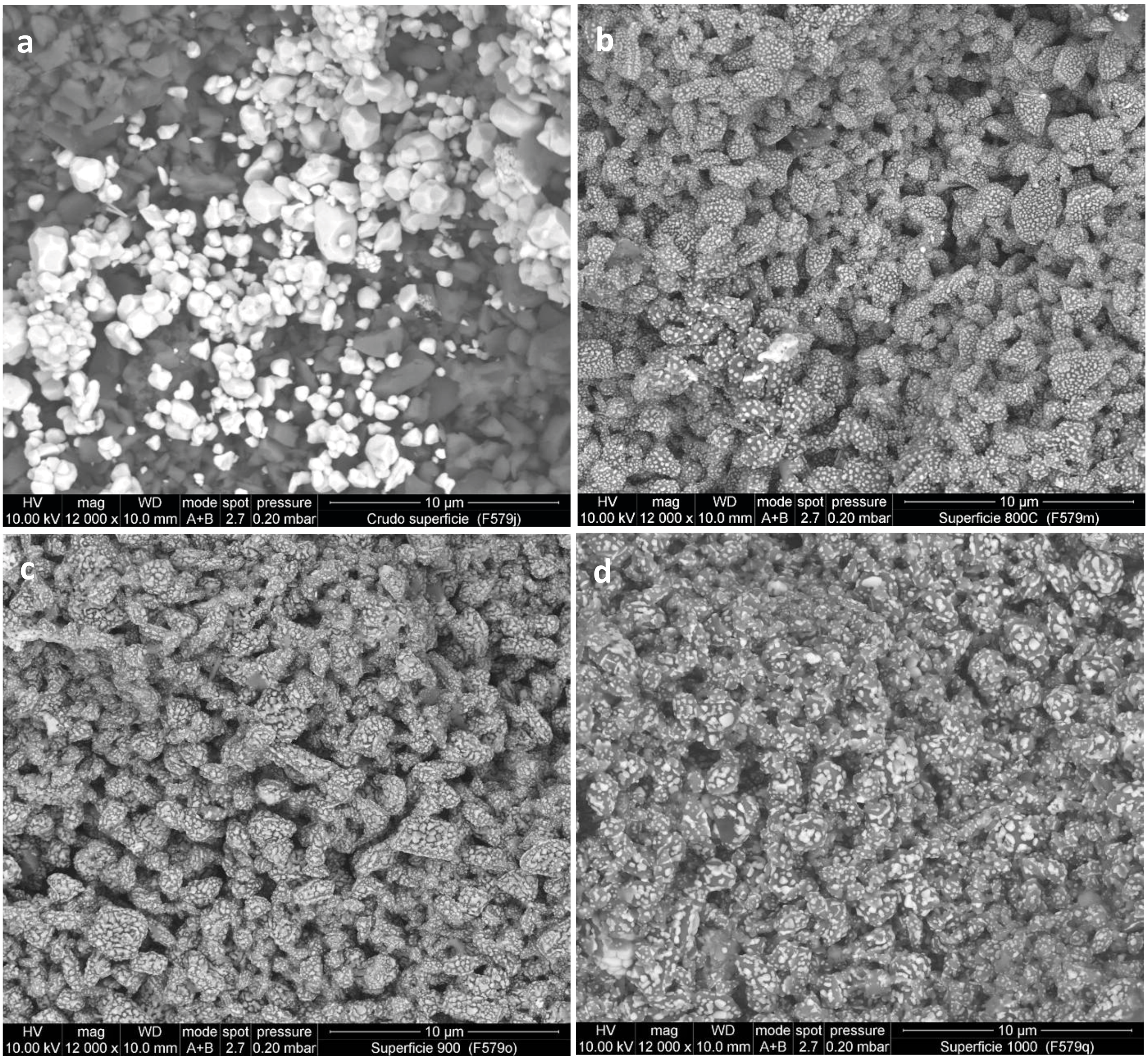

Figure 9. *Surface of the pieces obtained with frit C/3: (a) unfired; (b) 800 °C; (c) 900 °C; and (d) 1000 °C.*

5. CONCLUSIONS

The study on tungsten lustres enables the following conclusions to be drawn:

- The lustre effect is due to the formation of a surface layer of $CaWO_4$ by reaction between the calcium in the frit and the tungsten that is applied on the unfired glaze surface. The refractive index of $CaWO_4$ is 1.9 whereas that of a silica glass is of the order of 1.5, which is why interference phenomena occur when light impinges on and is partially reflected from the faces of the $CaWO_4$ surface layer. This interference is modified with the light angle of incidence, producing the decorative effect mentioned ("lustre", "nacre", "mother-of-pearl", or "iridescence").
- The intensity of the lustre effect increases as the crystal layer becomes more continuous, i.e. the greater the glassy surface area covered by the crystals.
- For this effect to take place, the crystal layer must be oriented and embedded in the fired glaze. In general, the crystals that form in a melt display preferential orientations, so that it is necessary for the crystals to form during firing of the piece. It was verified that the application of precursors on the surface of an unfired piece with frit C and subsequent firing did not generate the lustre effect. This was probably because of the random orientation of these crystals.
- When the evolution with temperature of pieces with C/3 frit on which WO_3 was applied was observed, it was concluded that the $CaWO_4$ formation mechanism took place by means of a solid–gas reaction. WO_3 begins to sublimate at 750°C, which is why its vapour must have been partly carried away by the atmosphere in the kiln and have partly reacted with the Ca in the frit. The reaction took place at the surface of the frit particles.
- It was verified that when the frit had a d_{90} of 40 μm, the reaction surface was not very high and allowed a surface layer of $CaWO_4$ to form that produced the lustre effect. In contrast, when the frit particles were small (d_{90}=3 μm) the reaction surface increased and formed a homogenously distributed, $CaWO_4$ crystal skeleton, which surrounded the frit particles (coating these particles). This skeleton generated a rigid structure ($CaWO_4$ crystals are very refractory), which prevented viscous flow sintering and consequently did not enable the surface film needed to produce the sought-after decorative effect to form.

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