MATT GLAZES IN TILES MADE BY FAST DOUBLE FIRING

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ABSTRACT

The matt appearance of certain glazes, obtained from frits that devitrify during heat treatment, depends strongly on the heat treatment. Temperature/time conditions are often inadequate to allow the devitrified crystals to grow sufficiently to provide the glaze with the matt texture, and thus give rise to glossy glazes. On other occasions, partial dissolution of the previously devitrified crystals occurs, consequently also producing glazes with a glossy appearance.

This study addresses the crystallisation in a frit with which matt glazes are obtained in fast double-fired tiles. The study shows that the phase responsible for the matt appearance is a calcium and zirconium double silicate, although initially other phases devitrify which are unstable at the peak temperature of the cycle. The crystals of the calcium and zirconium double silicate are star-shaped, with arms up to 15µm long. The crystallisation sequence and the temperature range in which the crystalline phases are stable, as well as the effect of the thermal cycle on the matt appearance of the resulting glazes, have been determined. The proportion and size of the crystals in the glaze were found to depend on the peak firing temperature and the cooling rate. Thus, the degree of mattness of glazes obtained with thermal cycles in which partial dissolution of crystals occurs at the peak firing temperature will vary with the cooling rate. A slow cooling will allow the crystals to grow and the glaze will be matter than the glaze obtained with fast cooling.

1 INTRODUCTION

Based on their optical characteristics, glazes are classified as transparent/ opaque and glossy/matt. Transparency/opacity depends on the refractive indices of the phases that make up the glaze, whereas gloss/mattness depends, in addition, on the roughness of the glaze surface. When light strikes a smooth surface it is reflected in specular form (the incident beam is reflected at an angle equal to the incident angle). In contrast, when the surface is rough, the incident light undergoes diffuse reflection, and is partly reflected in every direction. The fraction of light reflected in diffuse form and specular form depends on the roughness of the surface it strikes[1].

Matt glazes are heterogeneous materials, consisting of a glassy matrix that contains crystalline phases of relatively large size, which provide the surface with a certain roughness. They can be obtained from glazes comprising a frit or mixtures of frits with crystalline raw materials that dissolve partly or completely, with subsequent crystallisation during cooling[2,3]. Other types of matt surfaces are those obtained by abrading or chemically attacking glossy glasses[4], or those that stem from inadequate maturing of the glaze. In this last case the surface exhibits pores and sufficiently deep breaks to prevent surface cleaning, making these completely devoid of interest[5,3].

The frits used to obtain matt glazes are colloquially known as 'matt frits'. During firing of the glazed tile, these frits characteristically devitrify phases whose crystals grow readily, yielding glazes consisting of a glassy matrix in which large crystals (10-15μm) are immersed. Those crystals can provide and/or increase the apparent viscosity so preventing surface stretching.[6]

The crystalline phases that form in these glazes are usually silicates and/or aluminosilicates of Ca, Mg, Ba and Zn, and may include one or several of these elements. The most common phases in matt glazes are wollastonite[7,8], anorthite[9], diopside[10,11], cordierite[12], willemite[2] and celsian[13,14]. The degree of opacity of the resulting glazes will depend on the differences between the refractive indices of the devitrified phase and the glassy matrix. Zirconium is sometimes used to obtain an opaque matt glaze; this can be added as zircon to the glaze composition, or included in the frit composition[15,16].

The fact that matt glazes contain a high proportion of crystalline phases with moderate melting temperatures, except for celsian whose melting temperature is 1760°C, makes them very sensitive to the thermal cycle, which can cause partial dissolution of the crystalline phases, altering the surface texture and, hence, gloss[6]. In this study a frit has been formulated with Ca and Zr, with which matt glazes are obtained in double-firing processes. The sequence in which the phases crystallise has been determined, and the frit composition has been modified to extend the temperature range that allows obtaining glazes with the same degree of mattness.

2 EXPERIMENTAL

A frit (F1) containing Ca and Zr was prepared. Two further frits, F2 and F3, were obtained based on frit F1, appropriately modifying the composition to increase their fusibility. These frits enable producing matt glazes in fast double-firing thermal cycles. Frit F1 was characterised by differential thermal analysis (DTA) and a fusibility test in the hot stage microscope. The latter test was also performed on frits F2 and F3.

Each frit was used to prepare the respective glaze compositions (E1, E2 and E3) which, in addition to the frit, contained 8% kaolin by weight and the relevant additives (0.3% sodium carboxymethylcellulose and 0.1% sodium tripolyphosphate).

The mixtures of raw materials were wet milled in laboratory mills, until achieving a reject of 4% by weight on a 45μm sieve. The resulting suspensions were applied on previously fired, engobed wall tile bodies. After drying, the glazed pieces were fired in an electric laboratory kiln at a heating rate of 25ºC/min. to the peak temperature, followed by a dwell time of 6 min. at this temperature and cooling in the kiln. The peak temperatures tested ranged from 900 to 1200ºC. In order to study the effect of the thermal cycle cooling stage, in some of the firings, after the dwell time at peak temperature had elapsed, the pieces were withdrawn from the kiln and cooled in the ambient (quenching). Roughness and gloss of the resulting glazes were measured, and the glaze surface was observed in a scanning electron microscope (SEM).

The gloss measurement was performed with a RHOPOINT Statistical Novo-Gloss reflectometer. Ten gloss measurements were made at a 60º angle of incidence, and the arithmetic mean was then calculated.

Glazed surface roughness was determined from the topographic maps obtained with a Wyco NT 1100 optical profiler. The cut-off filter used for the calculation of the R_a parameter was 25μm. The R_a parameter corresponds to the arithmetic mean of the absolute values of the distance of the points that make up the profile to a mean line, and is the most representative parameter of the mean roughness of a surface.

In order to identify the crystalline phases that devitrified during firing of glaze E1, a suspension of the same glaze was prepared without sodium carboxymethylcellulose, and used to form cylindrical test specimens by casting. These test specimens were subjected to non-isothermal heat treatments at a heating rate of 25ºC/min. to the different peak temperatures, withdrawing the test specimens from the kiln when these temperatures had been reached. Isothermal treatments were also conducted at 950ºC, with different dwell times, withdrawing the test specimens from the kiln after the dwell time. X-ray diffraction (XRD) tests were performed on the fired test specimens, and their microstructure was observed with a SEM.

3 RESULTS AND DISCUSSION

3.1. CHARACTERISATION OF FRIT F1 AND GLAZE E1

The shrinkage curves of frit F1 and glaze E1, obtained by hot stage microscopy, are plotted in Figure 1. Table 1 details the values of the characteristic temperatures, obtained from this test. It can be observed that the presence of kaolin raises glaze shrinkage start by 40°C, generally shifting the whole curve towards higher temperatures.

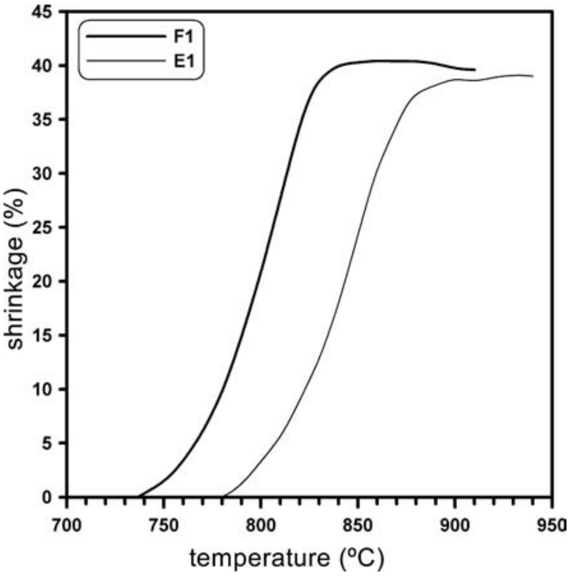

Figure 1. Shrinkage curves of frit F1 and glaze E1.

CHARACTERISTIC T	F1	E1
Shrinkage start T_{IC}	750°C	790°C
Shrinkage end T_{FC}	860°C	900°C
Softening T_R	890°C	940°C
Melting T_F	1190°C	1170°C

Table 1. Characteristic temperatures of frit F1 and glaze E1.

In the hot stage microscopy test it was observed that the test specimen went from softening to fusion without displaying a half-sphere or sphere shape. This could be due to the presence of crystals in the melt, acting as a framework and holding the shape of the test specimen approximately until the crystals fused. The sudden increase in the quantity of liquid phase when the crystals fuse causes the test specimen to collapse in a short range of temperatures.

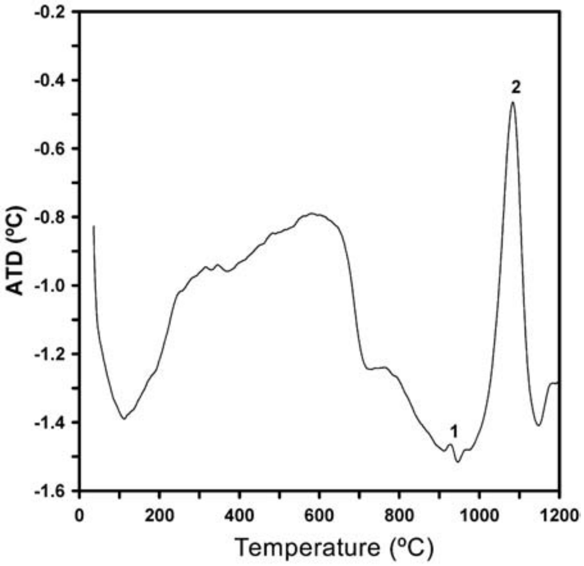

Figure 2. Differential thermal analysis of frit F1.

The differential thermal analysis of frit F1 (Figure 2) highlights the presence of two exothermic peaks, which correspond to two crystallisations (referenced 1 and 2), respectively peaking at 932°C and 1086°C (exactly between the detected softening and fusion temperatures in the hot stage microscope). The difference between these two peaks might be caused by a much greater second crystallisation, or because the second crystallisation is much more exothermic than the first.

3.2. STUDY OF DEVITRIFICATION IN GLAZE E1

In the XRD analysis of the glaze E1 test specimens, obtained by casting and treated at 25°C/min. to different maximum temperatures, two crystalline phases were identified: anorthite ($CaAl_2Si_2O_8$) and the calcium and zirconium double silicate ($Ca_2ZrSi_4O_{12}$). Figure 3 plots the variation of intensity in the characteristic peaks of the identified phases. This intensity is proportional to the content in these phases for the different samples, since the mass absorption coefficients are maintained. The notation CaZrSi corresponds to the calcium and zirconium double silicate, $Ca_2ZrSi_4O_{12}$.

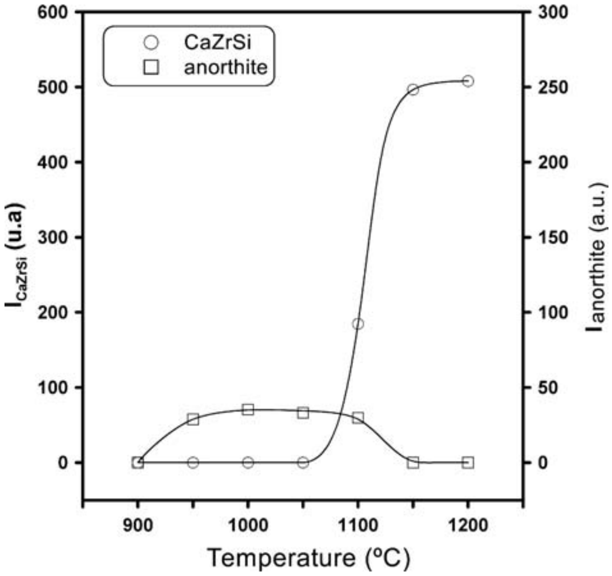

Figure 3. Intensity of the d_{hkl} reflections of anorthite and of the d_{hkl} reflections of the calcium and zirconium silicate.

At 900°C no crystalline phases are detected. The first phase to form is anorthite, which is stable in these glazes up to 1100°C, the temperature at which the calcium and zirconium double silicate is also detected. At 1150°C and 1200°C the only crystalline phase present in the glaze is $Ca_2ZrSi_4O_{12}$. Owing, on the one hand, to the size of the test specimens and, on the other, to their withdrawal from the kiln when peak temperature was reached without any dwell time at that temperature, the formation of crystalline phases in glazed tiles probably shifts to lower temperatures than those shown in Figure 3, since the applied glaze layer is much thinner. The results obtained from the SEM examination of the test specimens are analysed below.

For this, we prepared fresh fractures of the cast test specimens, treated thermally as set out at the beginning of this section. Figure 4 shows the appearance of the test specimens treated at 1000 and 1100°C. At 1000°C some dark crystals were observed, located at what was initially the edge of the frit particles, with high calcium content (anorthite), together with small white crystals of ZrO_2, which were in darker regions than the crystal-free glass, which indicates the local depletion of the melt in heavy elements (Zr). Test specimen microstructure at 1050°C matched that at 1000°C. At 1100°C the quantity of Ca-rich crystals had decreased greatly, the ZrO_2 crystals were larger and more numerous, and some large star-shaped crystals were observed, corresponding to $Ca_2ZrSi_4O_{12}$.

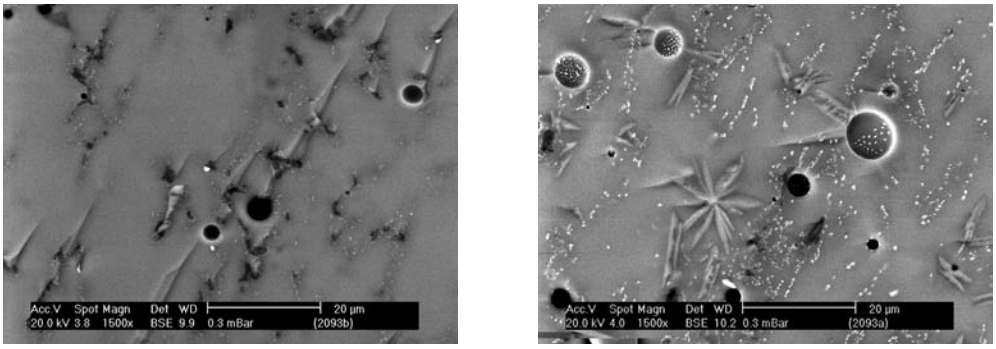

Figure 4. Fracture of the cast test specimens treated at 25°C/min. to 1000 and 1100°C.

In the test specimen treated at 1150°C (Figure 5), no anorthite crystals were detected; the $Ca_2ZrSi_4O_{12}$ crystals had grown greatly, some of which contained small ZrO_2 crystals, while acicular zircon crystals were also observed. At 1200°C the appearance of the test specimen was very similar, except that no ZrO_2 was observed, whereas zircon crystal quantity and size had increased.

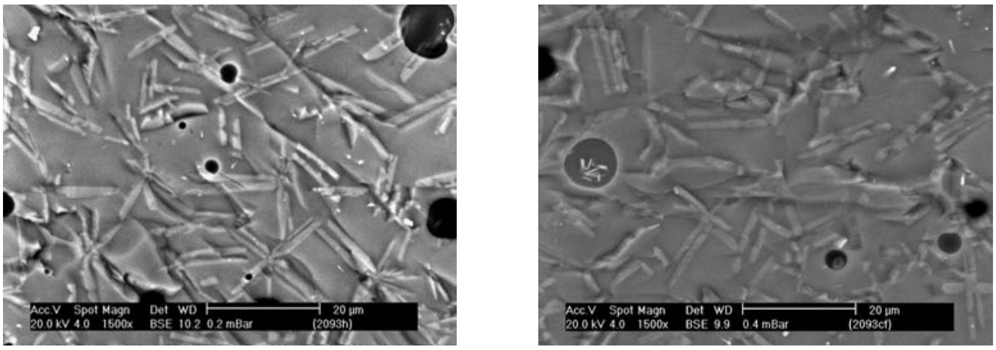

Figure 5. Fracture of the cast test specimens treated at 25°C/min. to 1150 and 1200°C.

After detecting anorthite and ZrO_2 in the SEM examination of the test specimens obtained at the lowest test temperatures, a series of isothermal experiments were conducted to establish how these phases evolved. Test specimens were prepared for this purpose by casting, and subjected to 950°C for different times. At 5 and 10 min. dwells at 950°C, no crystalline phases were detected by XRD. In the test specimen with a 15 min. dwell, the phases identified by XRD were anorthite and $Ca_2ZrSi_4O_{12}$. At 30, 45 and 60 min. the only detected phase was $Ca_2ZrSi_4O_{12}$.

SEM analysis of the cross-section of the test specimens with 5 min. treatment displayed anorthite crystals in what had initially been the surface of the frit particles. These are precisely the areas in which kaolin had been located, which favours anorthite formation by reacting with calcium in the melt. At 10 min. treatment small white ZrO_2 crystals were observed next to anorthite crystals. This could be because the formation of anorthite impoverishes the calcium melt, encouraging ZrO_2 devitrification. Incipient star-shaped $Ca_2ZrSi_4O_{12}$ crystals were also observed (Figure 6).

At 15 and 30 min. treatments the number of anorthite crystals decreased, while $Ca_2ZrSi_4O_{12}$ crystal quantity and size increased. The test specimens corresponding to 45 and 60 min. treatments quite resembled each other (Figure 7): only an isolated incidental anorthite crystal was observed, the $Ca_2ZrSi_4O_{12}$ crystals were very large and numerous, and small ZrO_2 crystals were detected, some of them located inside the $Ca_2ZrSi_4O_{12}$ crystals.

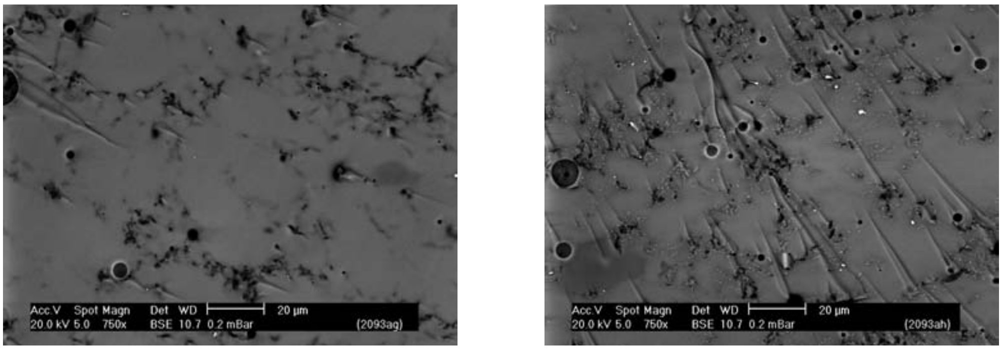

Figure 6. Fracture of the cast test specimens treated at 950°C for 5 min. and 10 min.

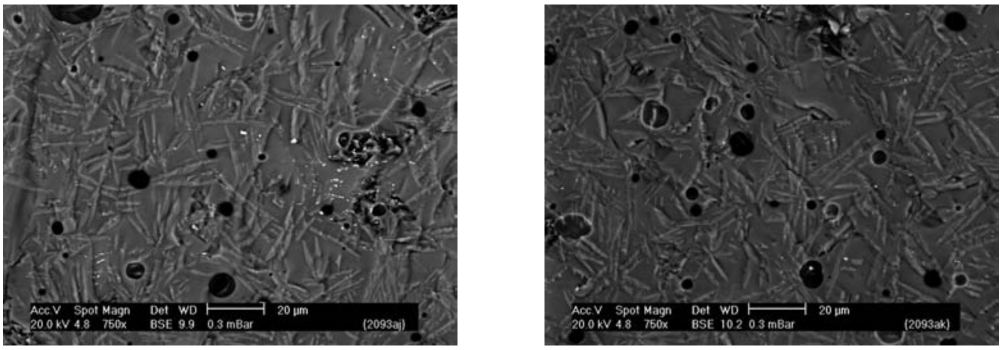

Figure 7. Fracture of the cast test specimens treated at 950°C for 45 min. and 60 min.

These results are consistent with those obtained in the non-isothermal experiments, and show that in these glazes anorthite is an unstable phase that dissolves when heat treatment temperature and/or time is increased.

3.3. EFFECT OF THE THERMAL CYCLE ON THE MICROSTRUCTURE OF THE GLAZES OBTAINED WITH THE E1 GLAZE

After identifying the crystallisation sequence in the glaze, the relation between the development of the crystalline phases and the appearance of the resulting glazes was determined by firing glazed test specimens in an electric laboratory kiln at different peak temperatures. Dwell time at peak temperature was 6 min. in all the cycles, and two types of cooling were tested: cooling in the kiln and quenching (withdrawal from the kiln after dwell time at peak temperature).

The variation of glaze gloss and roughness with peak firing temperature has been plotted in Figure 8. It shows that in the glaze obtained at 940°C, surface roughness is low and, hence, gloss is high. When T_{max} is raised, roughness increases owing to the crystals appearing at the surface, entailing a decrease in gloss. The roughness values are observed to be more sensitive to the changes in the glazed surface than the gloss values, since from 980°C on, there is a gradual decrease in roughness with the rise of T_{max}, whereas the gloss values hardly change.

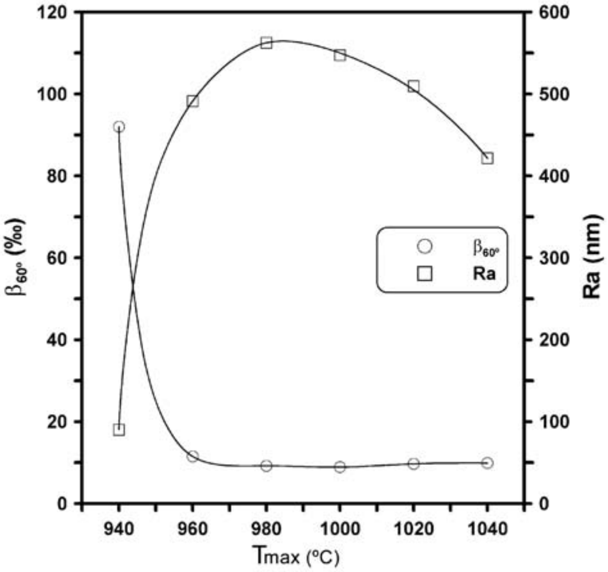

Figure 8. Variation of gloss and roughness of glaze E1 with heat-treatment T_{max}.

Figures 9 to 11 correspond to the surface of these glazes. At 940°C three crystalline phases were detected: anorthite (dark-coloured regions), zirconium oxide (glossy specks) and $Ca_2ZrSi_4O_{12}$ (grey star-shaped crystals). The small size of the crystals and, therefore, the small percentage of the surface they occupy, explain the high gloss of the glaze. At T_{max} = 960°C the number and size of ZrO_2 crystals had increased and were more defined due to a greater difference in composition to the residual glassy phase, which was poorer in zirconium. The calcium and zirconium silicate crystals had grown considerably, and their size was far greater than those of the other crystalline phases; this is why this phase is responsible for the matt appearance of the glazed surface.

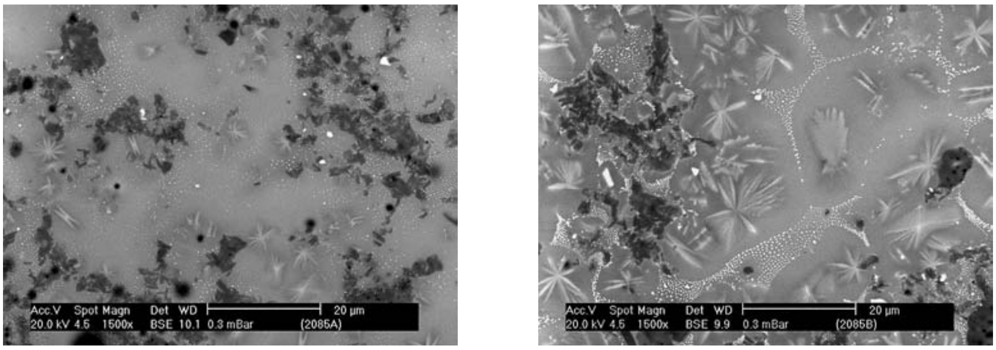

Figure 9. Surface of the glazes obtained at 940°C and 960°C.

At 980°C the calcium and zirconium silicate crystals had continued growing, hardly any anorthite was left and acicular zircon crystals were observed together with the zirconium oxide (whiter specks) (Figure 10). At T_{max} = 1000°C crystal density was very high and anorthite was no longer detected. Beyond this temperature the acicular zircon crystals increased in size and $Ca_2ZrSi_4O_{12}$ began dissolving, since in the glaze at 1040°C crystal density had diminished. This dissolution of $Ca_2ZrSi_4O_{12}$ crystals caused roughness to decrease, with the ensuing slight increase in glaze gloss at 1020°C (Figure 11).

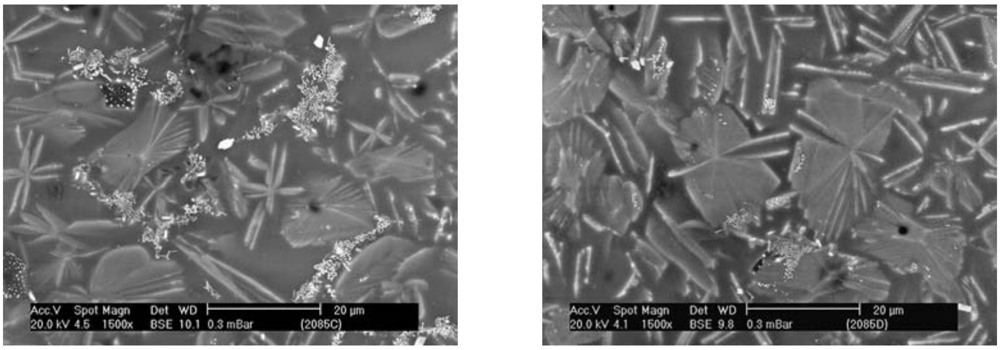

Figure 10. Surface of the glazes obtained at 980°C and 1000°C.

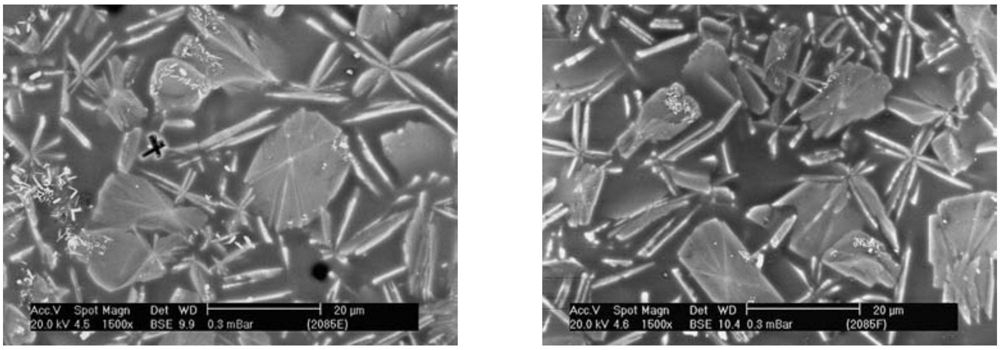

Figure 11. Surface of the glazes obtained at 1020°C and 1040°C.

If crystal dissolution takes place at peak firing temperatures, these crystals can grow again during cooling[6], provided the glaze resides long enough in the range of temperatures at which crystalline growth occurs. In order to verify the effect of the cooling stage on the thermal cycle, glazes were fired in an electric kiln at peak temperatures of 1000, 1040 and 1120°C, with two types of cooling: cooling in the kiln and quenching. Figure 12 plots the resulting glaze gloss values. It shows that the gloss of the glazes withdrawn from the kiln at T_{max} is higher than that of the glazes cooled inside the kiln. This is because, as indicated previously, during cooling crystalline growth takes place at temperatures above T_g. When the cooling is very fast, the crystals have no time to grow.

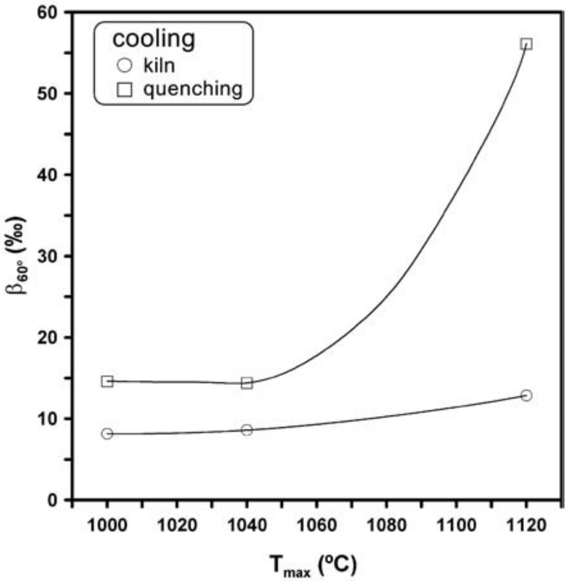

Figure 12. Gloss of the E1 glazes fired at different T_{max} and subjected to two different coolings.

Figure 13 displays the surface of the glazes obtained at T_{max} = 1120°C, with both tested coolings. It can be observed that crystal density is not very high in the piece subjected to quenching, i.e. during the 6 min. dwell at T_{max} an important fraction of the crystals that had devitrified in heating dissolves. In the piece cooled in the kiln, these crystals are observed to grow during cooling.

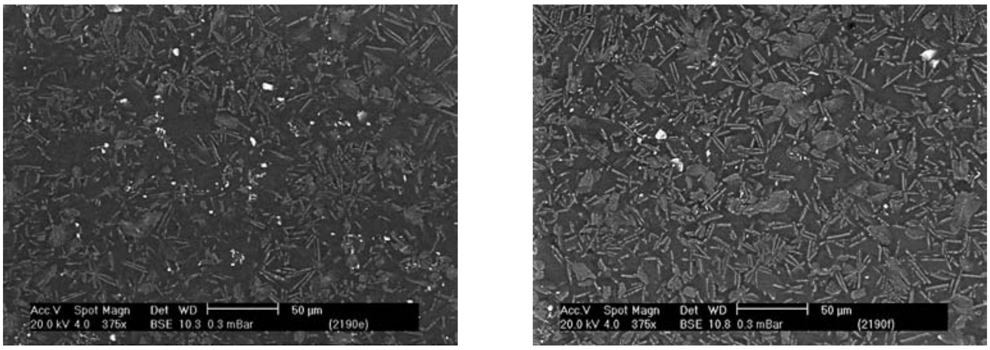

Figure 13. Surface of the glazes obtained at 1120°C. Left: quenching at 1120°C. Right: cooling inside the kiln.

3.4. INFLUENCE OF GLAZE COMPOSITION ON THE MICROSTRUCTURE OF THE RESULTING GLAZES

The fact that in the matt glazes, at certain firing temperatures, the devitrified crystals partly dissolve, possibly to grow again during cooling, means that the degree of mattness of these glazes depends on the thermal cycle. In order to determine the effect of glaze composition on the stability range, i.e. the temperature range in which gloss does not depend on the thermal cycle, we modified the composition of frit F1: specifically, two new frits were prepared, F2 and F3, in which the quantity of fluxing oxide was increased slightly at the expense of the elements that form $Ca_2ZrSi_4O_{12}$. The effect of these compositional changes on melt viscosity is depicted in Figure 14, which plots the sintering curves obtained in the hot stage microscope. These curves show a notable change has occurred in thermal behaviour, as frits F2 and F3 sinter more quickly and reach a greater degree of sintering than frit F1. However, after sintering end, the test specimens deformed almost immediately, unlike frit F1, which holds its shape across a wider range of temperatures.

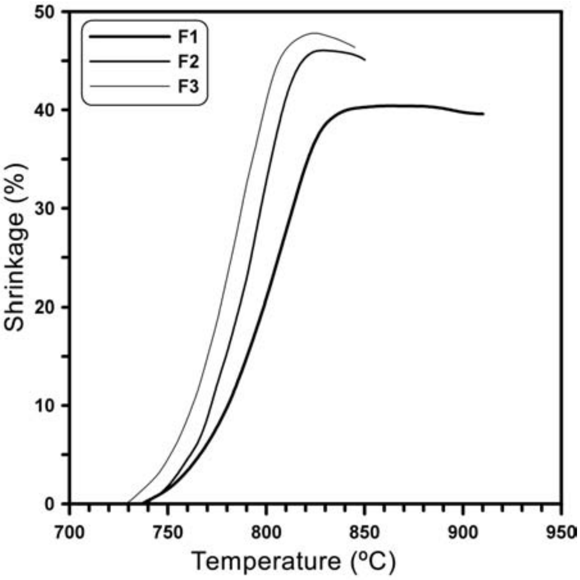

Figure 14. Sintering curves obtained in the hot stage microscope of frits F1, F2 and F3.

The new frits were used to prepare the corresponding glaze compositions (referenced E2 and E3), with which the experiment was repeated to verify the effect of the type of cooling described in the previous section. The resulting glazes were then characterised in terms of gloss and microstructure (SEM). It was verified that, in every case, the phase responsible for the matt appearance of the glazes was $Ca_2ZrSi_4O_{12}$. Figures 15 and 16 plot the gloss of the glazes obtained with the tested cooling cycles: cooling inside the kiln (Figure 15) and quenching (Figure 16).

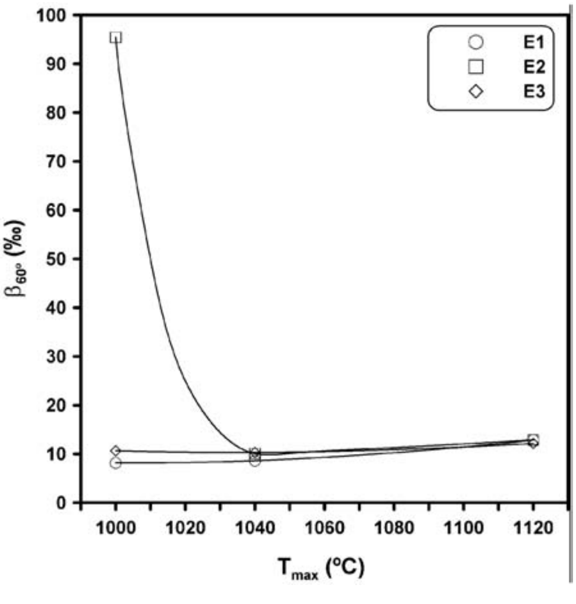

Figure 15. Effect of frit composition on glaze gloss. Cooling inside the kiln.

In glaze E1 at 1120°C the $Ca_2ZrSi_4O_{12}$ crystals have dissolved appreciably (increase in gloss in Figure 16), followed by growth during cooling (constant gloss in Figure 15), as remarked in the previous section.

The microstructure of the E2 glazes at 1000°C consists of small crystals, which is why gloss is high after both types of cooling. In these glazes the temperature range in which $Ca_2ZrSi_4O_{12}$ crystal size is sufficiently large for the glazes to be matt begins around 1050°C, and no appreciable dissolution has occurred at maximum test temperature (1120°C).

Finally, the E3 glazes hardly exhibit any variation in gloss in the studied range of temperatures, for the two tested types of cooling; they are, therefore, the most stable in the thermal cycle, in this range. The low gloss value at 1120°C with quenching indicates that crystal dissolution has not yet begun at this temperature.

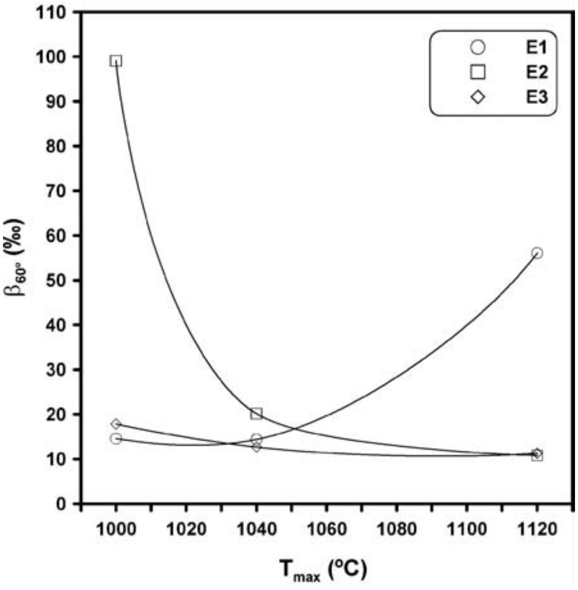

Figure 16. Effect of frit composition on glaze gloss. Cooling by quenching.

4. CONCLUSIONS

When a frit was used that yields matt glazes in fast double-firing processes, it was verified that the first crystalline phase to form during firing was anorthite, at what were initially frit particle surfaces. This phase then dissolved in the melt and was not detected in the final glaze.

The residual glass in the regions in which anorthite forms becomes poorer in calcium, causing supersaturation with ZrO_2, resulting in zirconium oxide crystallisation. The fact that this phase was not detected by XRD could be because it is present in a low quantity and, therefore, is below the detection limit.

Parallel to zirconium oxide crystallisation, a calcium and zirconium silicate ($Ca_2ZrSi_4O_{12}$) began to form, with star-shaped crystals that increased in size with temperature, up to 15μm. This crystalline phase is the main cause of the matt appearance of the glazes. The increase in $Ca_2ZrSi_4O_{12}$ crystal quantity and size reduced the devitrified ZrO_2, probably because it was used in calcium and zirconium silicate formation. The phases present in the glaze at the optimum firing temperature were $Ca_2ZrSi_4O_{12}$ and $ZrSiO_4$, which came from the transformation of the residual ZrO_2. At temperatures above the optimum firing temperature, the $Ca_2ZrSi_4O_{12}$ crystals began to dissolve, with the ensuing reduction in roughness and increase in the glaze gloss.

If partial dissolution of the devitrified crystals takes place at peak firing temperature, these crystals will grow again during cooling. In this case, the final appearance of the glaze will depend on the dwell time in the range of temperatures in which this crystalline growth occurs.

In order to determine the range of temperatures in which the glaze is stable, it is recommended to fire this at different maximum temperatures, and withdraw the piece from the kiln at these temperatures to avoid crystal growth during cooling.

By modifying the composition of the starting frit, we have displaced the range of temperatures in which $Ca_2ZrSi_4O_{12}$ devitrification occurred, thus obtaining sufficiently large crystals to produce a matt glaze, and avoiding their subsequent dissolution in the melt. The study shows that appropriate modification of the frit composition allows stabilising the $Ca_2ZrSi_4O_{12}$ against dissolution in the glassy phase at peak firing temperature, as a result of which final glaze gloss is quite independent of the thermal cycle.

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