# STUDY OF OPACIFICATION IN ZIRCONIUM CERAMIC GLAZES USED IN SINGLE-FIRED WALL TILE MANUFACTURE

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## ABSTRACT

A study was undertaken of the causes of opacification in glossy, white zirconium glazes, used in coating single-fired wall tiles, and the effect on opacity of the firing cycle these glazes undergo.

The study was performed using a zirconium frit that was subjected to differing heat treatments. The end opacity was then determined of the resulting glazes (measured as whiteness index), as well as the nature and proportion of the crystalline species they contained.

A direct proportionality was shown to exist between the crystallized zircon fraction (sole crystalline phase detected by XRD) in the glass, and its whiteness index. The maximum amount of crystallized zircon in the glaze was also found to lie quite close to the maximum attainable if all the zirconium in the starting frit were to crystallize as zircon.

## 1. INTRODUCTION

Some 40% of the glazed ceramic wall tiles currently being manufactured has glossy, opaque, white glaze coatings. The frits used to obtain these glazes vary in composition, depending upon the technique utilized in fabricating the wall tiles (traditional double firing, fast double firing, or single firing). Their $ZrO_2$ content usually ranges from 7 to 12% (in weight)[1].

The opacity of these glazes, which is related to their whiteness index, stems from the devitrification of zirconium crystalline phases (zircon and zirconia), which on having different refractive indices from the glassy phase containing them, give rise to reflections and refractions of incident light, which lower transparency. The opacity of glazes containing crystalline phases has been shown to relate to the number and size of the crystals present.

No studies have been found in the literature on the opacification of zirconium glazes used in single-fired wall tile manufacture, whose composition differs from those commonly utilized in double firing, on which several studies have been published [2-6]. It was therefore considered of interest to investigate the behaviour during firing, of the zirconium frits used in single firing, given the importance this technique has acquired of late in our country.

## 2. OBJECTIVE AND SCOPE

An intent has been made in this study to determine the causes of opacity in glossy, opaque, white zirconium glazes coating single-fired porous wall tile.

The study has also addressed the influence of the firing cycle to which the starting frits are subjected, on the opacity of the resulting glazes.

A series of experiments was programmed for this purpose, in which a zirconium frit was subjected to varying heat treatments, subsequently determining the whiteness index as a measure of opacity of the resulting glazes, as well as the nature and amount of the crystalline species they contained.

## 3. MATERIALS AND EXPERIMENTAL TECHNIQUE

### 3.1. MATERIALS

The study was performed using a frit fabricated by ESMALGLASS, S.A. Table 1 lists its main physico-chemical characteristics:

***Table 1.*** *Physico-chemical characteristics of the frit used.*

| | |
|---|---|
| Zirconium oxide content (weight percent) | 11.5 |
| Silicon oxide content (weight percent) | 57.9 |
| Other oxides | 30.6 |
| Crystalline phases detected by X-ray diffraction | None |
| Crystalline phases detected by SEM and analyzed by EDX | Zircon (*) |

(*) Some unmelted particles smaller than 20 µm.

### 3.2. SAMPLE PREPARATION

The experiments aimed at determining glaze opacity were performed with glazed test pieces.

The glaze was prepared by adding 5% kaolin, 0.2% sodium tripolyphosphate and 0.2% carboxymethyl cellulose (in wt) to the selected frit. The glaze suspension was applied by spray gunning onto a red-firing body, of the kind usually employed in single-fired ceramic wall tile manufacture, which had been pre-fired at 1100°C, a higher temperature than those used subsequently to fire the glaze applied to the piece, in order to obtain the final glaze coating.

By operating in this manner, the possibility of colour differences arising in the fired body, which might have biased the glaze whiteness index measurements, was thus avoided, since the maximum firing temperature of the heating cycle used could have influenced the colour of the fired body.

The glazed test pieces were fired in an electric laboratory kiln, with heating cycles resembling those in Figure 1, at maximum firing temperatures of 900°C, 950°C, 1000°C, 1050°C and 1100°C.

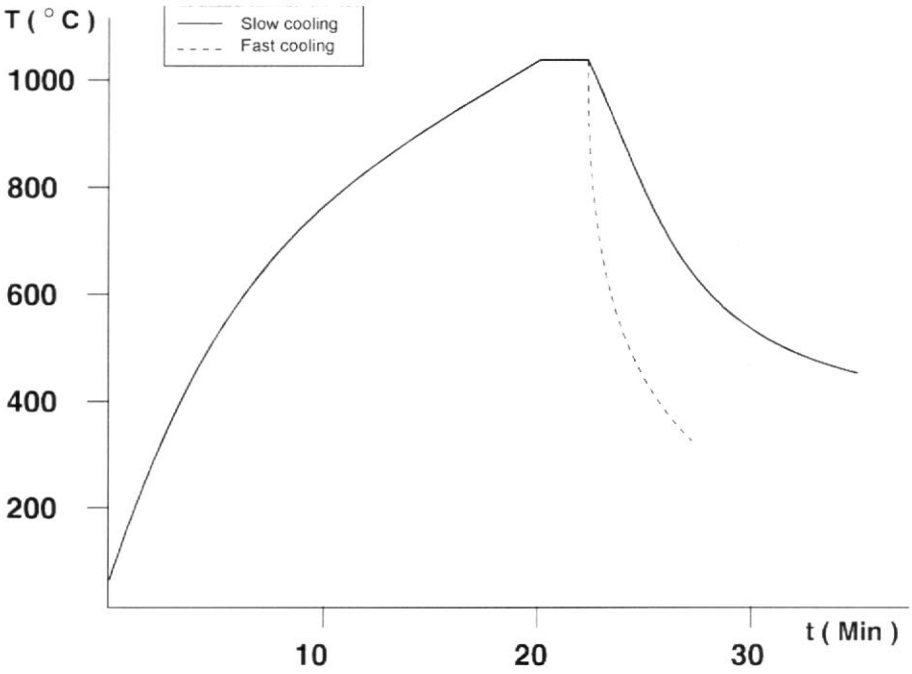

***Figure 1.*** *Firing cycles used.*

The experiments performed to quantitatively determine the fraction of the crystalline species present in the glazes, were carried out with cylindrical frit test pieces, formed by casting, from slips prepared by wet grinding the selected frit. On placing these test pieces on a fired ceramic body, they were subjected to a heat-treatment cycle like the one with the fast cooling step in Figure 1, in an electric laboratory kiln.

## 3.3. DETERMINATIONS PERFORMED

### 3.3.1. Examination by scanning electron microscopy

The microstructure of the glazes obtained were examined with a scanning electron microscope (SEM). The test pieces were prepared by embedding cross sections of the glazed pieces in an epoxy resin.

### 3.3.2. Whiteness index

Opacity of the glazes was assimilated to their greater or lesser degree of whiteness. Whiteness and yellowness indices were measured with a Dr Lange LMF-3 tricolour colorimeter. The sample to be measured was illuminated by a C standardized light source, corresponding to average daylight.

Lighting took place at a 45° angle, reflected light being detected by three photoreceptors (with red, green and blue filters). Glaze whiteness was measured from the reflected light reaching the photoreceptor with the blue filter.

To narrow the margin of experimental error, the whiteness index of four samples was determined in each experiment, averaging the values obtained. Glaze thickness was measured in each sample before assessing this property, since it is affected by this thickness. The samples whose glaze thickness deviated considerably from the average value were rejected.

### 3.3.3. X-ray diffraction

The quantitative determination of the crystalline phases in the samples tested, was performed by X-ray diffraction, using the procedure involving successive additions with an internal standard [7]. Corundum was chosen as the internal standard.

## 4. RESULTS AND DISCUSSION

### 4.1. INFLUENCE OF THE FIRING CICLE ON GLAZE OPACITY

Table 2 details the average values of the whiteness and yellowness indices of the glazes obtained in the two kinds of heat-treatment cycle described in Figure 1. Figure 2 shows a plot of the variation of the whiteness and yellowness indices of the glazes in function of the maximum temperature of the firing cycle they were subjected to, in the two kinds of heat-treatment cycle tested.

**Table 2.** *Whiteness ($R_z$) and yellowness ($Y_i$) index values for the maximum temperatures and kind of cooling tested.*

| Temperature (°C) | Type of cooling | $R_z$ (%) (*) | $Y_i$ (%) (**) |
|---|---|---|---|
| 900 | slow | 31.5 | 16.6 |
| 950 | slow | 60.1 | -0.5 |
| 1000 | slow | 70.7 | -1.7 |
| 1050 | slow | 66.9 | -3.8 |
| 1100 | slow | 68.7 | -3.0 |
| 900 | fast | 30.1 | 16.8 |
| 950 | fast | 60.4 | 1.0 |
| 1000 | fast | 70.3 | -3.4 |
| 1050 | fast | 69.9 | -1.9 |
| 1100 | fast | 68.8 | -2.0 |

(*) Reflectance to the blue filter (450 nm).
(**) Yellowness index.

This figure shows that for both kinds of heat-treatment cycle, the evolution of the whiteness and yellowness indices follow opposite paths, so that at the temperatures at which the glaze reaches its maximum whiteness index values, lie the lowest yellowness index values and vice versa.

The fact that no appreciable differences are observed among the values of these indices in the glazes obtained with the two kinds of heat-treatment cycle tested, would seem to indicate that the phenomenon giving rise to whiteness in the glaze almost wholly develops in the heating step of the firing cycle, since this coincides in both heat-treatment cycles, whereas that of the cooling step differs.

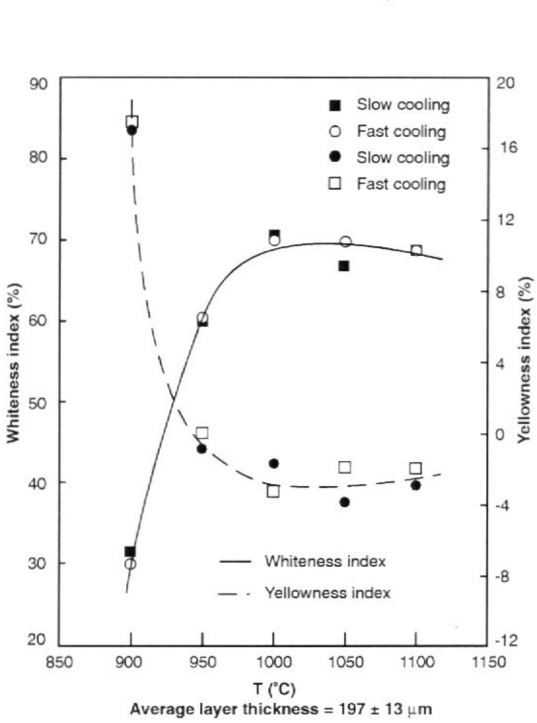

***Figure 2.*** *Variation of the whiteness and yellowness indexes with maximun firing temperature, in the firing cycles used*

## 4.2. VARIATION IN CRYSTALLINE-PHASE CONTENT WITH FIRING CYCLE MAXIMUM TEMPERATURE

The only crystalline phase detected by X-ray diffraction in the glazes obtained was zirconium silicate. Should other different crystalline phases also be present, their amounts must lie below the boundary value the instrument can detect.

Table 3 details the zirconium silicate mass fraction in the cylindrical test pieces formed from the frit by slip-casting, after firing them at different maximum temperatures. The firing schedule used in this case involved fast cooling since, as indicated above, crystal formation took place during the maximum temperature and heating steps.

***Table 3.*** *Variation of the crystallized zircon mass fraction in the glaze with maximum temperature of the firing cycle used*

| T (°C) | $x_c$ | $x_c/x_{c,\ max}$ |
|---|---|---|
| 900 | 0.081 | 47.6 |
| 950 | 0.134 | 78.7 |
| 1000 | 0.162 | 94.4 |
| 1050 | 0.159 | 93.4 |
| 1100 | 0.153 | 89.8 |

The same table includes the values of the ratio between zircon crystal content in the glaze ($x_c$) and the content there would be if all the zirconium in the starting frit composition were to turn into zircon crystals ($x_{c,max} = 0.17$).

The values of the crystallized zirconium silicate fraction in the glaze have been plotted versus the maximum temperature of the firing cycle used to obtain it in Figure 3. The crystallized zircon fraction ($x_c$) increases with glaze maximum firing temperature, peaking at 1000 °C. At slightly higher temperatures (1050 - 1100 °C), $x_c$ decreases slightly, perhaps due to some of the zircon dissolving in the glassy phase. The comparison between the values of $x_c$ obtained and those that would be obtained if all the zirconium in the starting frit had crystallized as zircon, suggests that when the maximum temperature of the firing cycle coincides with the most suitable glaze maturing temperature (1000 - 1100 °C), the proportion of this phase which crystallizes will lie very close to the maximum possible amount.

## 4.3. MICROESTRUTURE OF THE GLAZES OBTAINED

It was observed by means of the EDX technique that the crystals present in the glazes consisted of silicon and zirconium, which confirmed the XRD findings, that is, that they mainly consisted of zircon. This does not exclude the possibility of there being a small zirconium oxide fraction, undetectable by XRD owing to the amount involved.

The photograph in Figure 4 shows that qualitatively the zircon crystal fraction in the glaze, at the lowest temperature tested (900°C), is very small. Between 900 and 1000°C (Figs. 5 and 6), the crystal fraction increases as temperature rises, with a slight growth in crystal size. On exceeding 1050 °C (Figures 7 and 8), there is a slight increase in crystal size and a slight drop in the number of crystals per unit surface area of the photographed glaze. These findings match those obtained by XRD, set out above (Table 4 and Figure 3).

## 4.4. RELATIONSHIP BETWEEN THE WHITENESS INDEX OF GLAZE AND ITS ZIRCON CRYSTAL PERCENTAGE

The variation in glaze opacity (expressed as the whiteness index) and its crystallized zircon mass fraction have been plotted versus maximum temperature of the firing cycle in Figure 9. Both properties are observed to vary in parallel fashion with maximum temperature, showing they are closely related.

In order to determine the nature of this relationship, the average whiteness index values of the glazes obtained, at the different maximum temperatures tested, were plotted versus those corresponding to the crystallized zirconium silicate fractions found in Figure 10. The points obtained satisfactorily fit a straight line.

It may therefore be stated that for the zircon crystal sizes obtained in the experiments described in this paper (< 10μm), the whiteness index of the resulting glaze is directly proportional to the crystallized zircon mass fraction it contains.

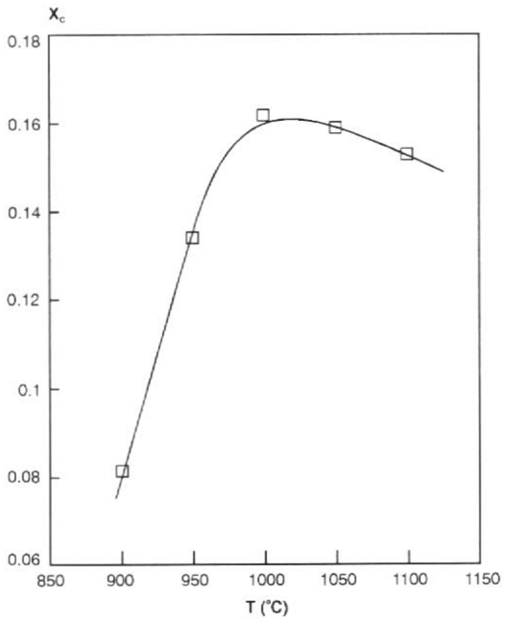

**Figure 3.** *Influence of firing cycle maximum temperature upon the crystallized zircon fraction in the resulting glaze.*

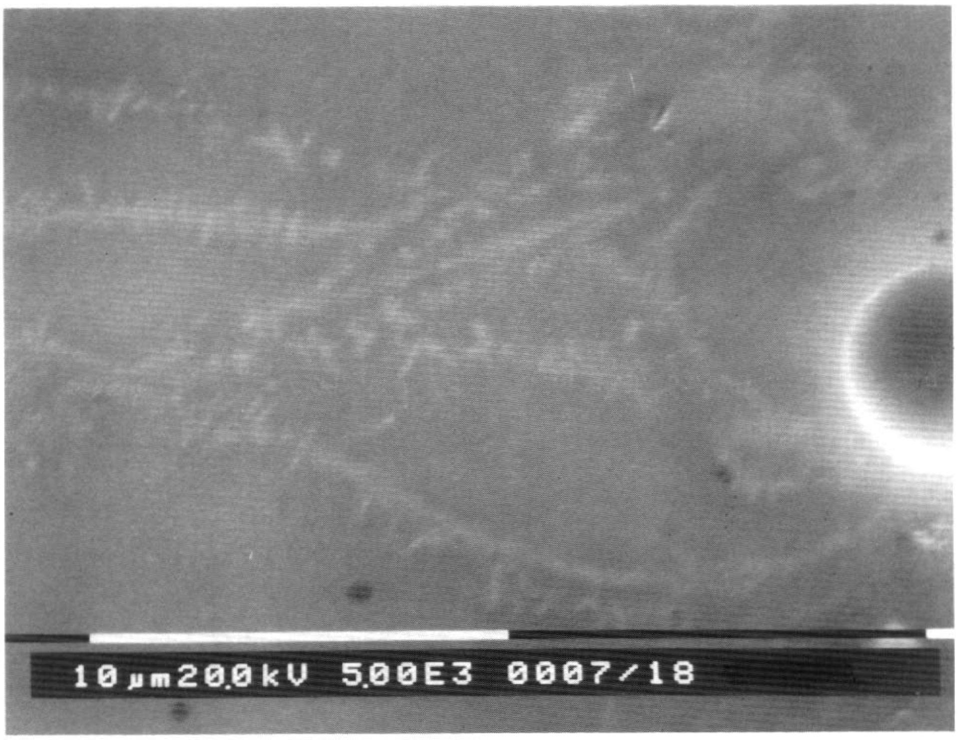

**Figure 4.** *Photograph of the microstructure of the glaze fired at a maximum temperature of 900°C.*

***Figure 5.*** *Photograph of the microstructure of the glaze fired at a maximum temperature of 950°C.*

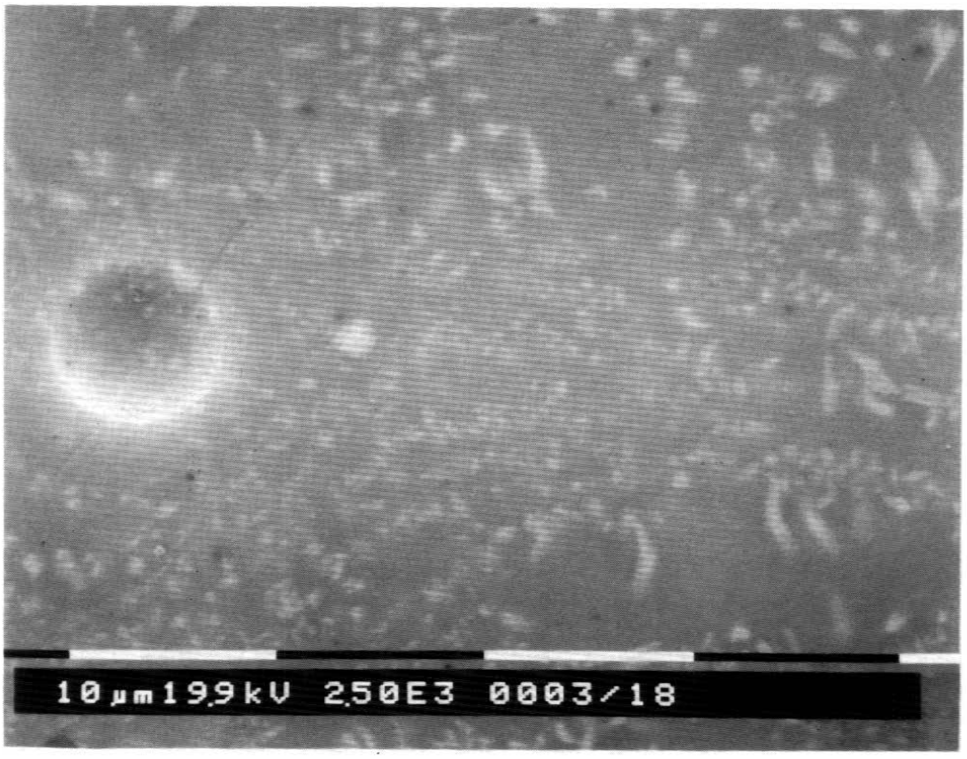

***Figure 6.*** *Photograph of the microstructure of the glaze fired at a maximum temperature of 1000°C.*

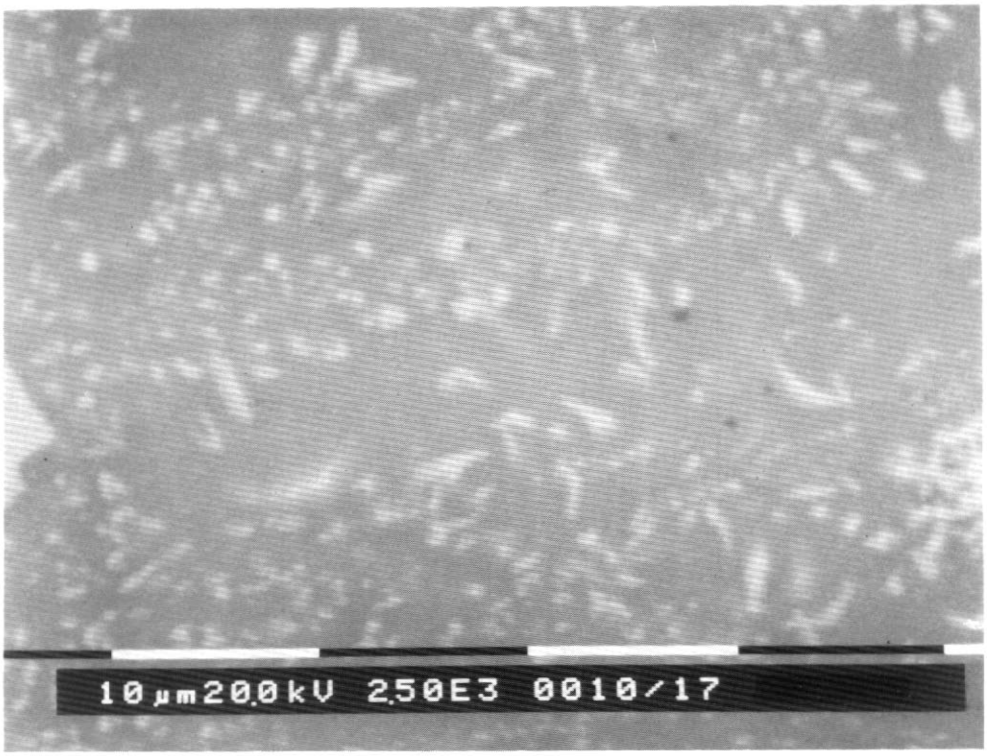

***Figure** 7. Photograph of the microstructure of the glaze fired at a maximum temperature of 1050°C.*

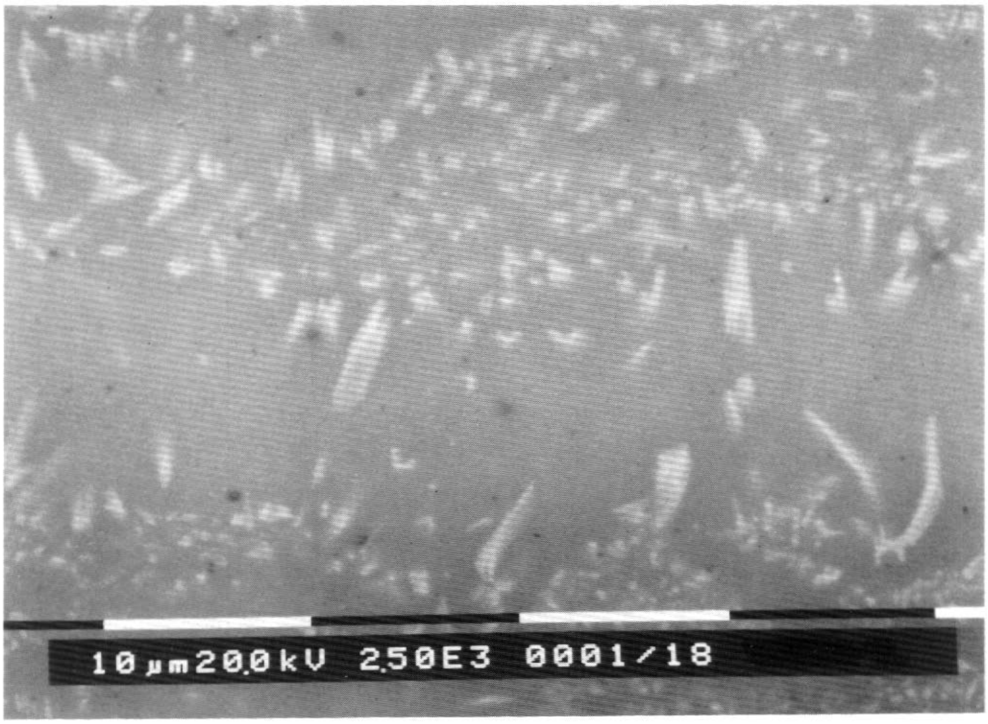

***Figure 8.** Photograph of the microstructure of the glaze fired at a maximum temperature of 1100°C.*

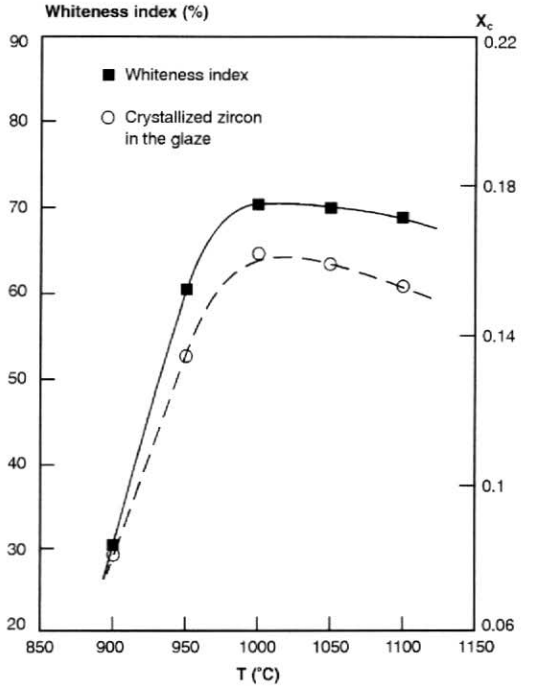

*Figure 9.* *Variation of the whiteness index of the glaze and its crystallized zircon fraction with maximum firing temperature*

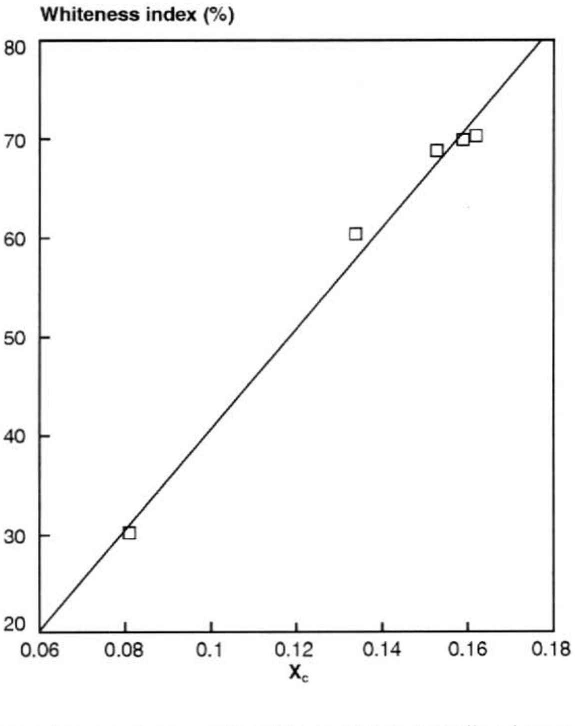

*Figure 10.* *Variation of the whiteness index of the glaze with its crystallized zircon fraction.*

## 5. CONCLUSIONS

The following inferences may be drawn from the results obtained in this study:

- The sole crystalline phase detected by XRD in the glazes obtained is zircon.
- Zircon crystallization virtually takes place wholly during the heating step of the firing cycle.
- The optimum interval of maximum firing temperatures for zircon crystallization, in the glaze prepared from the studied frit, lies between 1000 and 1100°C.
- The interval of maximum firing temperatures at which the opacity of the glaze prepared from the studied frit optimizes, coincides with the interval at which zirconium silicate crystallization maximizes.
- There is a direct proportionality between the crystallized zircon fraction in the studied glaze and its whiteness index, which substantiates the close relationship between both.
- The maximum crystallized zirconium silicate percentage in the glaze lies very close to the attainable maximum if all the zirconium in the starting frit were to crystallize as zircon.

## 6. REFERENCES

[1] AMOROS, J.L. "Glazes for Floor and Wall Tiles. Evolution and Perspectives". Proceedings of II World Congress on Ceramic Tile Quality. 69-100. Castellón. Spain. 1992.

[2] BOOTH, F.T.; PEEL, G.N. "The Principles of Glaze Opacification with Zirconium Silicate". Trans. Brit. Ceram. Soc. 58(9), 532-564, 1959.

[3] JURINE, H. "X-Ray Investigation of Glazes Containing Zirconia". "Science of Ceramics". Vol. I. Ed. STEWART, G.H. Academic Press. London and New York.35-49, 1962.

[4] SEHLKE, K.H.L.; TAUBER, A. "A High-Temperature X-Ray Diffraction Study of Zircon-Containing Glaze Frits". Trans. Brit. Ceram. Soc. 68(2), 53-56, 1969.

[5] KVYATKOVSKAYA, K.K.; GRYM-CRZHIMAILO, O.S.; MITROKHIN, V.S. "The Crystallization of Zircon in Glazes". Steklo i Keramica, 12, 24-25, 1974.

[6] GRUM-GRZHIMAILO, O.S.; KVYATKOVSKAYA, K.K.; KONDRASHEVA, E.F. "Fusible Zircon Glazes Based on Glassfiber Waste". Steklo i Keramika. (1), 27-28, 1992.

[7] MONSHI, A.; MESSER, P.F. "Double Dilution X-Ray Diffraction Method for Quantitative Phase Analysis of Multiphase Systems", Brit. Cer. Proc., 42, 201-212, 1989.