STUDY OF SOME VARIABLES INFLUENCING GLOSS IN GLAZES OBTAINED FROM FRIT AND TUNGSTIC OXIDE MIXES

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ABSTRACT

One of the decorative effects obtained in tiles is the so-called mother-of-pearl effect. In the finished product, this effect involves regions having higher gloss than the rest of the piece, which also exhibit variations in light reflection according to the angle of incidence.

A study was undertaken, using a screen-printing paste of the kind utilized in obtaining single-fired wall tiles with the mother-of-pearl effect, to determine the nature of the fired screen-printed films, and the influence the WO_3 content in the screen-printing paste and the firing cycle the piece undergoes, have on this decorative effect.

The mother-of-pearl effect was shown to be due to the presence of scheelite crystals ($CaWO_4$), formed by reaction between the WO_3 and the CaO contained in the frit. It was furthermore established that the gloss of the screen print solely depended on the fraction of the surface occupied by crystals and the gloss of the matrix containing these dispersed phases.

The intensity of this decorative effect was observed to increase with the WO_3 content of the screen-printing paste and to decrease on raising firing temperature of the piece and/or dwell time at this temperature. A simple procedure was developed to assess the intensity of the mother-of-pearl effect from the specular reflection measurements of the screen-printed and unprinted surfaces of the pieces obtained.

1. INTRODUCTION

Multiple decorative surface effects are currently being obtained by screen-printing applications in wall tiles, such as the so-called mother-of-pearl effect. In the finished product, this effect involves regions having much higher gloss than the rest of the piece, and which also exhibit variations in light reflection according to the angle of incidence. These variations entail visually detecting shades in the screen print on changing the viewing angle.

The fine layers of material selectively coating just part of the glazed wall tile are obtained by screen-printing a paste of suitable composition and viscosity on the unfired base glaze layer in the glazing operation. The screen-printing paste consists of a homogeneous mix containing suitable proportions of an organic binder, small particle-size tungstic oxide and preground frit.

Although tungstic oxide had been in use in small amounts (<4% in wt) in ceramic artware to obtain certain decorative effects in glazes with a high lead content [1], no study has been found in the literature on the nature of thin glaze films with high gloss containing tungstic oxide, which are used in preparing glazes with the so-called mother-of-pearl effect, or on the influence that the WO_3 content and firing cycle have on this decorative effect.

2. OBJECTIVES

This experimental work was undertaken, using a screen-printing paste of the kind utilized in obtaining single-fired wall tiles with the mother-of-pearl effect, with the following objectives:

i) Determining the nature of the thin glaze film resulting from firing the applied screen-print.

ii) Studying the influence that the percentage of tungstic oxide in the screen-printing paste and the heat treatment, to which the pieces with this application are subjected, have on the intensity of the decorative effect obtained and on some glaze properties directly related to this effect.

iii) Attempting to obtain a quantitative relationship between the properties determining the intensity of this effect and the microstructural characteristics of the glaze surface.

iv) Intending to assess the intensity of the mother-of-pearl effect, from the measurement of one or more easily quantifiable properties of the glaze surface.

3. EXPERIMENTAL

Different screen-printing pastes were prepared by following a procedure resembling the industrial one from mixes of a frit from ESMALTES CERAMICOS TORRECID, S.A. and tungstic oxide. The percentage of WO_3 in these mixes was 4, 6, 8 and 12% expressed as kg WO_3/100(kg WO_3+kg frit). The organic binder used was the same in all the experiments and the proportion was kept constant in the different screen-printing pastes.

These pastes were screen-printed on unfired wall tile bodies, on which an engobe as well as a base glaze layer had already been applied. The same frit that had been utilized in preparing the screen-printing paste was used as the base glaze. The pieces obtained were subjected to different heat-treatment cycles, modifying maximum firing temperature (T_c) and dwell time at that temperature (t_c), in an electric laboratory kiln (Figure 1).

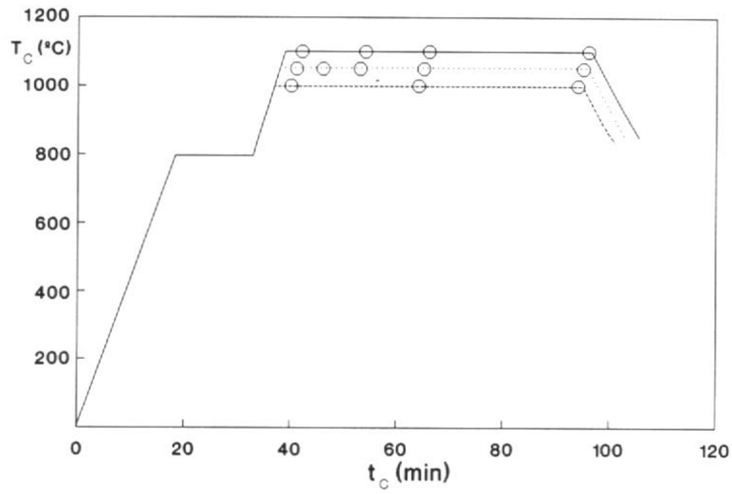

Figure 1. *Firing cycles used.*

Specular gloss was measured in the fired pieces at 60° [2], at the screen-printed ($ß_s$) and unprinted surfaces ($ß_b$), according to standard ASTM C584-81 [3]. This parameter was selected on observing that the gloss values measured in the screen-printed region ($ß_s$) increased with the WO_3 content in the screen-printed paste, analogously to the visually appraised intensity of the mother-of-pearl effect. Four measurements were performed at each of the surfaces examined. The scattering, expressed as the coefficient of variation, was less than 1%.

Glaze microstructure was examined by scanning electron microscope (SEM). The surface of the screen-printed area in each fired piece was examined with an optical microscope, determining the fraction of the total examined area occupied by crystalline phases (A_W), by an image analyzer [4][5]. Fifty measurements were carried out on each of the screen prints so that the values of A_W would be representative of the whole surface area. The scattering in the A_W values found, expressed as the coefficient of variation, never exceeded 5%.

In order to determine the nature of the crystalline phases forming in firing the screen-printing paste, cylindrical test pieces were prepared by slip-casting in a mould with a diameter of 1 cm and 1 cm thick, from an aqueous suspension of a mix of frit and tungstic oxide (12% WO_3). On drying, the test pieces were heat-treated in an electric laboratory kiln at a heating rate of 10 °C/min, until different maximum temperatures were reached. The crystalline phases in the fired test pieces were identified by X-ray diffraction (XRD), while SEM was used to examine their surface and interior microstructure.

4. RESULTS

4.1. MICROESTRUCTURE OF THE SCREEN-PRINTED FILM

On inspecting the surface of the screen-printed areas by SEM, in pieces prepared with varying WO_3 contents (Figure 2), and fired by identical heat treatment, (glassy or crystalline) phases were detected of a light shade, dispersed in a darker glassy matrix, suggesting marked differences in composition between both phases. These dispersed phases were not observed at the surface of the unprinted piece (base glaze).

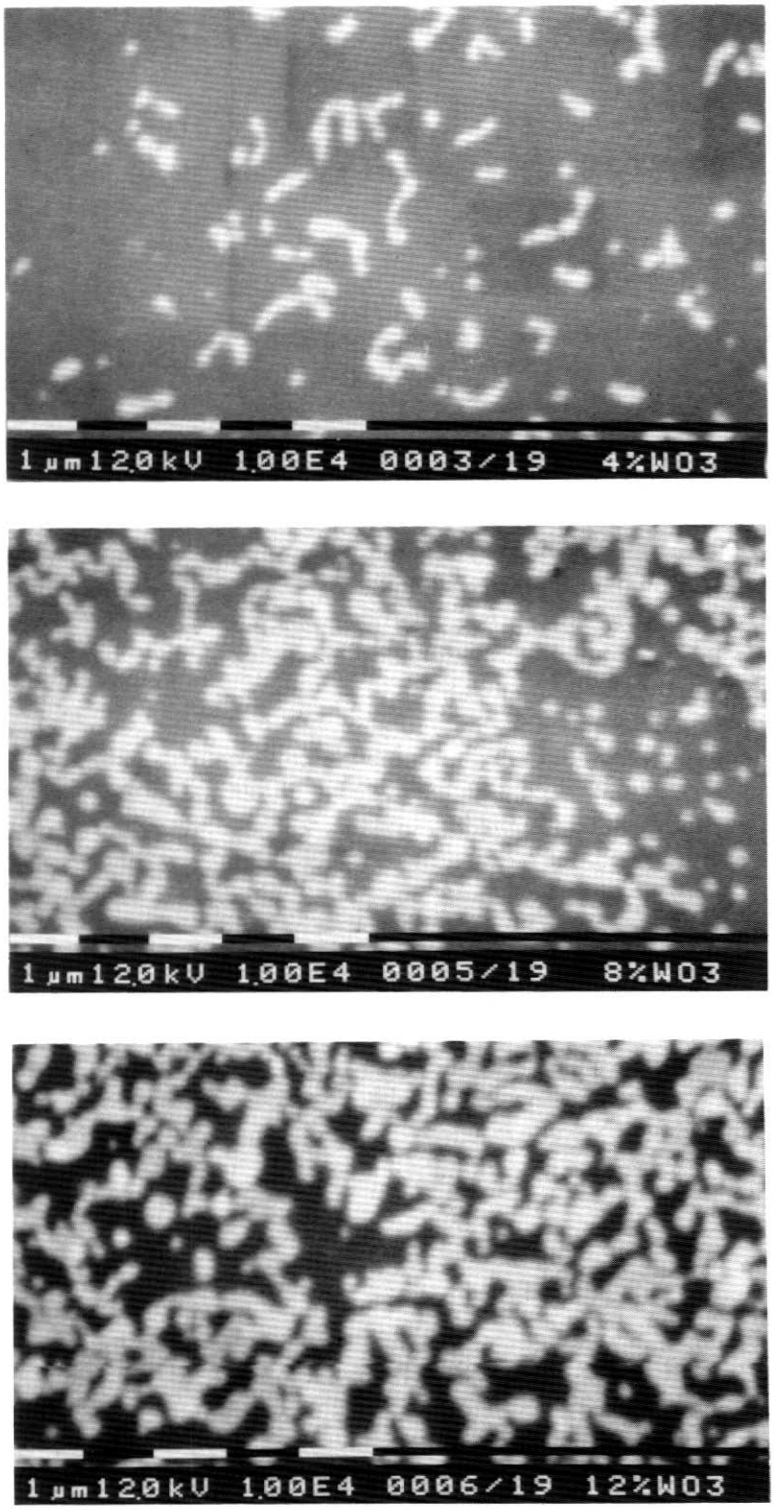

Figure 2. *Effect of WO_3 content in the screen-printing paste on microstructure of the resulting surface (T_c=1100°C; t_c=3 min)*

EDX microanalysis showed that the dispersed phases mainly contained tungsten and calcium, whereas the glassy matrix was free of tungsten and contained a smaller amount of calcium.

In order to determine the nature of these dispersed phases, X-ray diffraction tests were run on test pieces formed by casting and fired at different maximum temperatures (1000, 1050, 1100 and 1150°C) at a heating rate of 10°C/min. The diffractograms obtained only exhibited the peaks corresponding to scheelite ($CaWO_4$). This mineral has an adamantine gloss, high density (6 g/cm^3), a high refractive index (1.92) and crystallizes in the form of tetragonal dipyramids [6].

On comparing the SEM microphotographs of the screen-printed surfaces (Figure 2) obtained with varying WO_3 contents, following the same heat-treatment cycles, the surface area occupied by crystalline aggregates is observed to increase with WO_3 content, without any appreciable change in the size of the aggregates.

However, on studying the microphotographs of the screen-printed surfaces obtained using the same composition (WO_3=8%), following different heat-treatment cycles (Figure 3), the surface area occupied by crystalline aggregates is observed to decrease, while their size increases as maximum temperature and/or dwell time at this temperature rise.

4.2. INFLUENCE OF THE WO_3 CONTENT IN THE SCREEN-PRINTING PASTE AND FIRING CYCLE OF THE PIECE ON SOME CHARACTERISTICS OF THE RESULTING SURFACE.

4.2.1. Effect of the WO_3 content

In order to determine the effect of this variable on the visual perception of the decorative effect, on the gloss of the screen-printed surface ($ß_s$) and on the screen-printed surface fraction occupied by crystals (A_W), four screen-printing pastes were prepared with WO_3 contents of 4, 6, 8 and 12 kg WO_3/100(kg WO_3+kg frit), which after being applied were fired at a maximum temperature of 1100°C, with a 3 min dwell at this temperature.

On visually examining the fired pieces, the higher the WO_3 content in the screen print was, the more intense the gloss of the screen-printed surface with a mother-of-pearl appearance was observed to be.

In order to quantitatively determine this effect, measurements were performed of the gloss values of the screen-printed surface ($ß_s$) and of the base glaze surface, which did not contain WO_3 ($ß_b$).

On plotting the values of $ß_s$ versus the WO_3 content in the screen prints (Figure 4), a straight line with a positive slope is obtained, whose intercept coincides with the base glaze gloss value.

These findings would appear to indicate that an increase in WO_3 in the starting composition increases the screen-printed surface fraction occupied by $CaWO_4$ crystals (A_W) in the same proportion, entailing a parallel rise in surface gloss ($ß_s$), given the high gloss of this crystalline phase. To substantiate this assumption, the values of A_W were determined for each of the screen-printed surfaces. On plotting the values of A_W versus the corresponding WO_3 values of the screen-printing paste, a direct proportionality was shown to exist between the fraction of the screen-printed surface area occupied by $CaWO_4$, formed in firing, and the WO_3 content of the starting composition (Figure 5). Furthermore, on plotting the values of $ß_s$ versus A_W, the gloss of the screen print ($ß_s$) also increases proportionally with A_W, as expected (Figure 6).

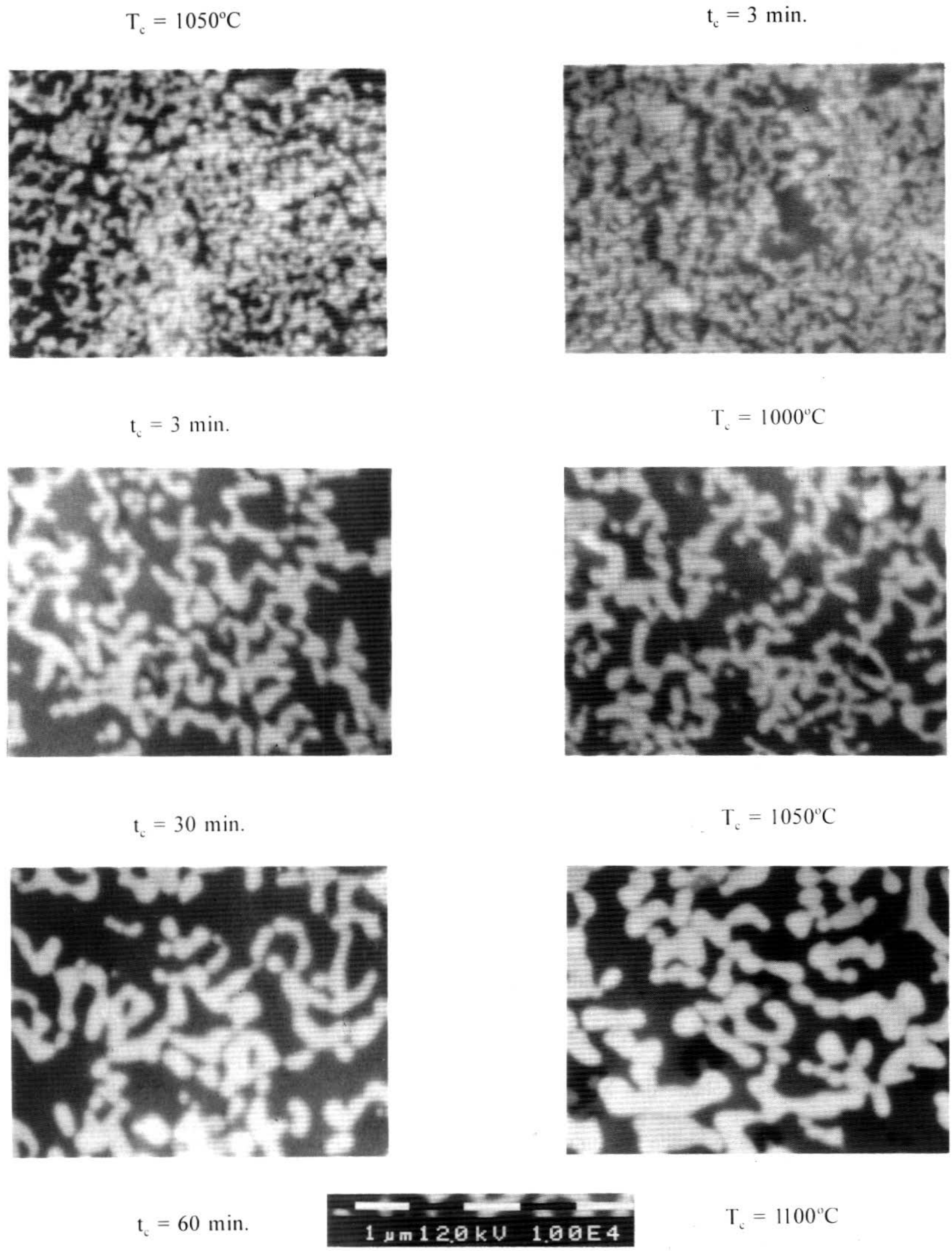

Figure 3. *Influence of maximum firing temperature (T_c) and dwell time at this temperature (t_c) on microstructure of the resulting screen-printed surface. WO_3 content = 8%*

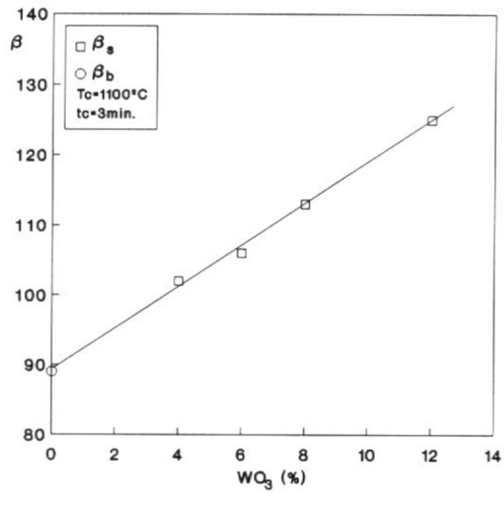

Figure 4. *Variation of screen-printed surface gloss (β_s) with WO_3 content. Base glaze gloss: β_b.*

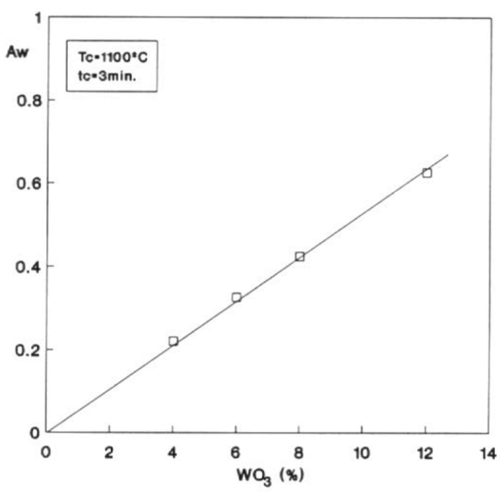

Figure 5. *Relationship between the surface fraction occupied by crystalline phases (A_W) and the WO_3 content in the screen print.*

4.2.2. Influence of the heating cycle

One sole screen-printing paste was used in this series of experiments with a WO_3 content of 8 kg WO_3/100(kg frit+kg WO_3). After glazing and screen printing the pieces, they underwent varying heat-treatment cycles (Figure 1) modifying maximum firing temperature (T_c) and dwell time at this temperature (t_c).

It was observed in the fired pieces that the lower the maximum firing temperature of the piece and/or dwell time at this temperature were, the more intense the mother-of-pearl effect was. However, the piece fired at 1000°C for 3 min exhibited a rough surface with numerous pinholes.

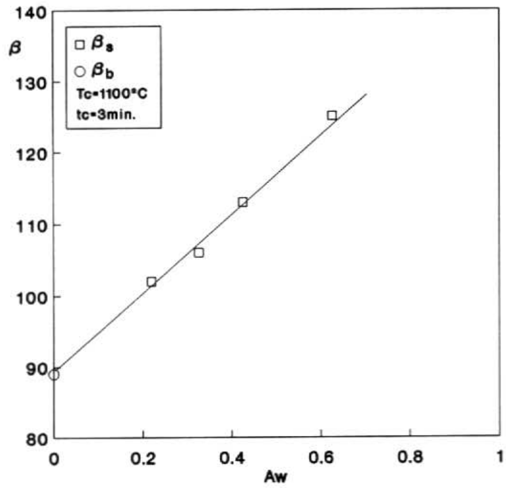

Figure 6. Relationship between screen-printed surface gloss (β_s) and the surface fraction occupied by crystals (A_W). Base glaze gloss: β_b.

Figure 7 shows a plot of the gloss values (β_s) and the values of the surface area fraction occupied by $CaWO_4$ crystalline aggregates (A_W), measured at the screen-printed surface, versus dwell time at maximum temperatures of 1000, 1050 and 1100°C.

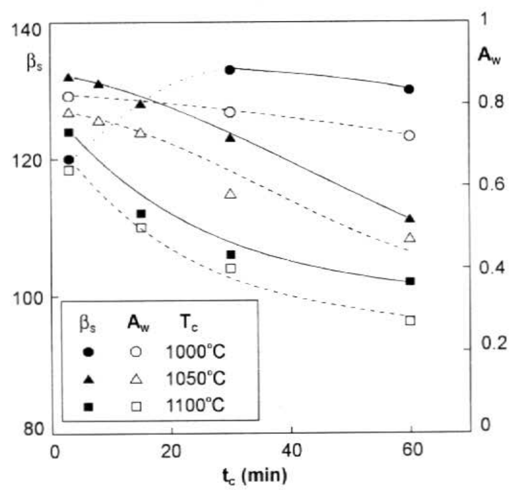

Figure 7. Influence of T_c and t_c on screen-printed surface gloss (β_s) and the fraction occupied by crystals (A_W). WO_3 content = 8%

Except for the piece fired at 1000°C for 3 min, the values of β_s and A_W are observed to decrease, following the same trend, as maximum firing temperature and/or dwell time at this temperature increase. These results again indicate a close relationship between A_W and β_s. The fact that the value of β_s corresponding to the piece fired at 1000°C for 3 min is unusually low, is due to excessive roughness of the glaze surface.

The decrease in the values of A_W with the increase in maximum firing temperature (T_c) and/or dwell time at this maximum temperature (t_c), is due to growth of $CaWO_4$ crystals and/or crystalline aggregates in this phase (Section 4.1), which tend to lower their surface area.

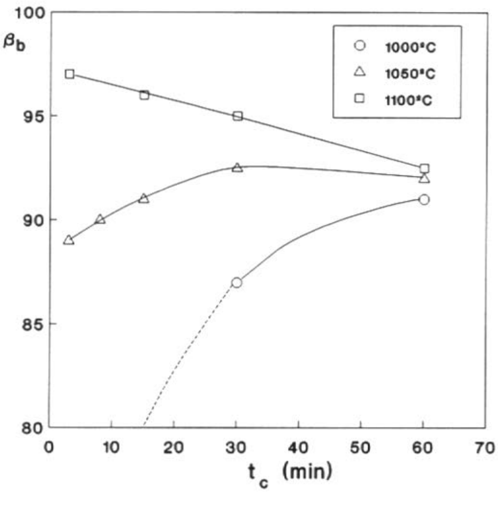

Figure 8. *Influence of maximum firing temperature (T_c) and dwell time at this temperature (t_c) on base glaze gloss (β_b).*

4.3. RELATIONSHIP BETWEEN SCREEN-PRINTED SURFACE GLOSS (β_s) AND THE AREA FRACTION OCCUPIED BY $CaWO_4$ (A_W)

In order to attempt to establish this relationship, gloss in the screen-printed area (β_s) was assumed to be the sum of two contributions: one owing to the presence of $CaWO_4$ surface crystals, which must be proportional to the gloss of these crystalline aggregates (β_W) and to the area fraction they occupy (A_W), and the other corresponding to the glassy matrix in which these crystals are dispersed, which must also be proportional to the gloss of the glassy matrix containing these dispersed crystals (β_m) and to the area fraction it occupies ($1-A_W$). Thus:

$$\beta_s=\beta_W.A_W+\beta_m(1-A_W) \qquad (1)$$

As the glassy matrix has the same chemical composition as the base glaze, the gloss corresponding to both surfaces must be assumed to be the same ($\beta_m=\beta_b$), so that Equation (1) can be rewritten:

$$\beta_s=\beta_W.A_W+\beta_b(1-A_W) \qquad (2)$$

$$\beta_W.A_W=\beta_s-\beta_b(1-A_W) \qquad (3)$$

According to Equation (3), the contribution to the gloss of the screen-printed surface as a result of the presence of $CaWO_4$ crystalline aggregates ($A_W\beta_W$) can be computed from the easily measurable values of β_s, β_b and A_W. Furthermore, if the assumptions are correct, on plotting the values of parameter $\beta_s-\beta_b(1-A_W)$ against the values of A_W, experimentally determined for all the screen-printed surfaces, a straight line should be obtained of slope β_W.

The values of $\beta_s-\beta_b(1-A_w)$ were computed from the base glaze surface gloss values (β_b), experimentally determined in the pieces fired with differing heating cycles (Figure 8), and those of β_s and A_W (Figs. 6 and 7). On plotting the values of this parameter versus those corresponding to A_W (Figure 9) a straight line is obtained through the origin, confirming the assumptions made. The slope of this straight line, corresponding to the gloss of the $CaWO_4$ crystalline aggregates, yields a value of 143.

With a view to substantiating the validity of the proposed model, the values of $ß_s$ calculated from Equation (2) have been plotted in Figure 10 against the experimentally obtained ones. There is shown to be good agreement between the calculated and the experimentally obtained values, bearing in mind the error involved in determining A_W and $ß_s$.

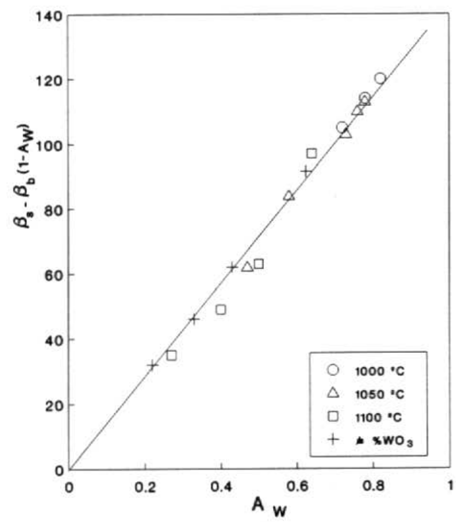

Figure 9. Fit of the experimental results to Equation (3).

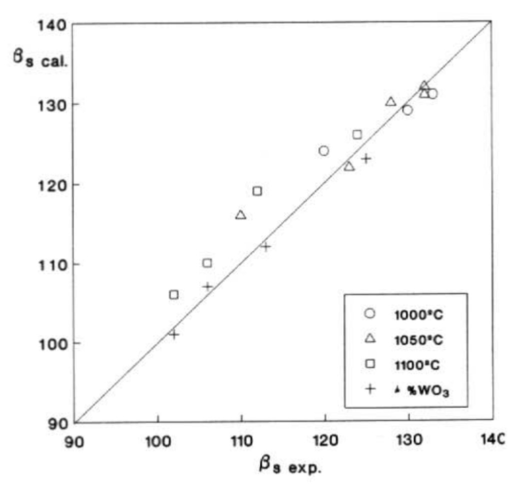

Figure 10. Comparison between the experimental results and those calculated by Equation (2).

4.4. EVALUATION OF THE INTENSITY OF THE DECORATIVE EFFECT (ΔB). INFLUENCE OF SOME VERIABLES ON ΔB

Taking into account that the greater the difference in gloss (ΔB) between the screen print ($ß_s$) and the base glaze ($ß_b$) is, the greater is an observer's visual perception of a screen print with a mother-of-pearl gloss, it was considered appropriate to use this parameter (ΔB) to assess the intensity of this decorative effect.

To substantiate the validity of this estimative parameter (ΔB), different observers visually examined all the pieces obtained by modifying the heating cycle and the WO_3 content in the starting composition, in order to rate the pieces according to the intensity of the effect. Although in many cases differences could not be visually established between the pieces, good agreement was found between the visually established rating and the one obtained using $\Delta\beta$ as a measurement parameter.

Figure 11 shows a plot of the variation of $\Delta\beta$ versus dwell time at maximum temperature (t_c), for maximum temperature values (T_c) of 1000, 1050 and 1100°C.

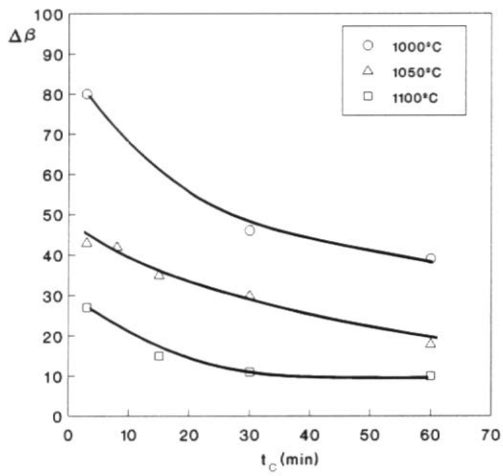

Figure 11. *Influence of maximum firing temperature (T_c) and dwell time at this temperature (t_c) on the intensity of the decorative effect ($\Delta\beta$).*

A considerable drop is observed in the intensity of the mother-of-pearl effect with the rise in firing temperature (T_c) since, with the increase of this variable, the gloss of the screen print decreases (Figure 7), as a result of a reduction in surface area of the $CaWO_4$ crystalline groupings, and base glaze gloss increases (Figure 8). A drop in the intensity of the mother-of-pearl effect is also observed with an increase in dwell time at firing temperature (t_c), while the lower the firing temperature is, the greater is this effect (curve slope). This behaviour is a result of the evolution that the area fraction occupied by crystals (A_W) and base gloss (β_b) undergo with t_c. Thus, at 1000°C, an increase in t_c entails a small drop in A_W (Figure 7) and a considerable rise in β_b, so that $\Delta\beta$ decreases quite markedly with this variable. However, at 1100°C, although A_W drops appreciably with an increase in t_c and, thereby so does β_s, base gloss (β_b) decreases only slightly with this variable, so that the influence of t_c on the intensity of the decorative effect ($\Delta\beta = \beta_s - \beta_b$) is less than at lower temperatures.

Figure 12 depicts the influence of the WO_3 content in the screen-printing paste on the intensity of the decorative effect. It shows that $\Delta\beta$ increases proportionally with the WO_3 content owing to a parallel rise in the surface area fraction of $CaWO_4$ crystals (A_W), as base gloss is not modified (β_b).

5. CONCLUSIONS

It was shown that the mother-of-pearl gloss in thin glaze films obtained from a screen-printing paste containing WO_3 is due to the presence of surface crystals of scheelite ($CaWO_4$), formed by the reaction between WO_3 and CaO in the frit.

The screen print gloss values were shown to depend solely upon the values of the surface fraction occupied by $CaWO_4$ crystalline aggregates and the value of the base glaze gloss. This relationship is independent of the operating variables used (WO_3 content, firing temperature and time).

The gloss of the screen-printed surface and the intensity of the mother-of-pearl effect increase with the WO_3 content in the screen-printing paste and decrease on lowering firing temperature and/or dwell time at this temperature.

A simple method has been developed to assess the intensity of this decorative effect from the specular reflection measurement values at the surface of the screen-printed and unprinted areas of the pieces.

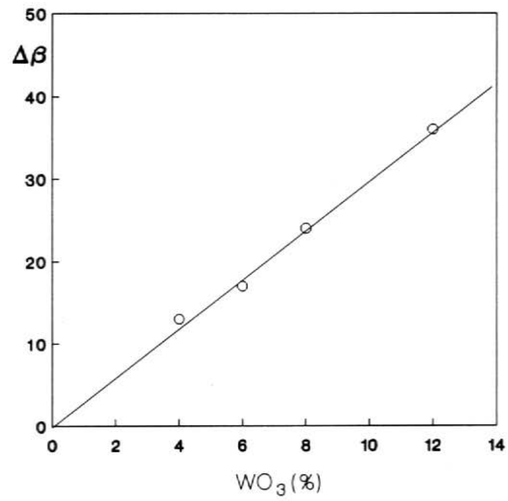

Figure 12. *Influence of WO_3 content in the screen print on the intensity of the decorative effect.*

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