DEVELOPMENT OF TiO$_2$ WHITE GLAZES FOR CERAMIC TILES: INFLUENCE OF FRIT MELTING AND GLAZE APPLICATION

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ABSTRACT

Based on a previous work, the objective of this study was to determine the effect of melting and glazing conditions of an anatase glaze used to promote white opacity in ceramic tile coatings. An anatase frit (10wt% TiO_2) was melted at 1,480°C and 1,530°C for 60min and 90min and quenched in water. Each frit was ground (30min) in eccentric mill with the addition of 10% kaolin, 0.2% sodium tripolyphosphate, 0.2% carboxymethylcellulose and 30% water, forming glaze slurries with 1.80g/cm³ density and viscosity of 100s in cup Ford n°4. The glazes were applied in layers of 0.4mm thickness over previously engobed tiles. The tiles were fired at 900°C, 1,000°C, 1,100°C and 1,190°C for 40min in a laboratory roller kiln. The colour of all the glazes was analyzed by spectrophotometry (400nm to 700nm) and the formed phases by x-ray diffraction (XRD CuKα) and scanning electronic microscopy (SEM). The results showed the glaze fired at 1,100°C obtained from the frit melted at 1,530°C for 90min formed a totally white glaze with great coating capacity. The results of scanning electron microscopy and X-ray diffraction revealed that the opacity is caused by tiny rutile crystals developed as function of melting and application temperature.

1. INTRODUCTION

Traditionally, industrial glazes for ceramic tiles use zircon or zirconia as opacity agents for coating, the former being much more commonly used due its lower cost. However, even when using large quantities of zirconia, the best results are not always obtained, showing that zirconia only yields a white coating when used in large quantities. The use of titanium oxide as a white coating is not a novelty; it has been used for decades to glaze porcelains and metals. However, there is a belief in the tile industry that TiO_2 only produces a yellowish opacity and it is not adequate for use in white coating glazes. Crystallites of TiO_2 formed during firing generate opacity; however, they do not yield white coatings [1-3] if impurities (Fe, Cr, etc.) are present in the raw materials, producing non-white coats [2-8]. Some studies have tried to predict the rutile to anatase concentrations in TiO_2-opacified coats as a function of time and temperature [7]. Anatase crystallization, rutile crystallization and the conversion of anatase to rutile, besides solubility factors (similar to the precipitation of salts from solutions), could be used to predict crystal concentrations under most conditions, except for short times and low temperature conditions, but the observed colour data did not correlate well with the observed, or predicted, crystalline concentration data [4-6]. Titanite crystals devitrify from the frit in the glaze composition during tile firing, but minor impurities (Fe, Cr, etc.) present in the glaze composition can produce non-white coats. Titanite, also known as sphene, is a calcium titanium silicate that forms flattened wedge-shaped crystals, being an isostructural titanium form that can incorporate transition metal cations; this system has been explored for colouring applications [7-12].

2. EXPERIMENTAL PROCEDURE

For the preparation of the white titanium frit, borate, potassium feldspar, calcite, titanium oxide (anatase), kaolin, flat glass, quartz and dolomite were used as raw materials. Table 1 shows the chemical analysis of the raw materials used in the frit formulation made by X-ray fluorescence spectroscopy (XRF, molten sample). The raw materials, except anatase, were crushed in a laboratory eccentric mill (500mL, alumina) for 30 minutes. After grinding, each raw material was mixed according the frit formula. After mixing the raw materials, formulations of 1.5kg were melted in alumina crucibles in the melting temperatures of 1,480°C and 1,530°C in two treatment periods of 60min and 90min in gas furnace, in order to determine the effect of melting conditions on the opacity of the frits. In sequence, each frit was poured into water.

(%) Mass fraction	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	LOI
Ulexite	17.8	4.2	0.0	1.3	21.7	1.4	1.3	3.2	0.1	8.0
K feldspar	64.1	10.0	0.0	0.1	0.1	0.1	11.9	3.0	0.3	0.7
Calcite	3.8	0.1	0.0	0.0	52.3	0.2	0.0	0.6	0.1	43.2
Anatase	-	-	98.5	-	-	-	-	-	-	1.0
Kaolin	47.6	37.8	0.0	0.3	0.1	0.0	0.6	0.1	0.1	13.5
Flat glass	72.8	0.0	0.0	0.2	8.0	3.8	0.3	14.2	-	0.0
Quartz	90.7	0.0	0.1	0.0	0.0	-	-	-	-	0.1
Dolomite	1.7	0.3	0.0	0.1	31.6	19.8	0.1	0.0	0.0	46.2

Table 1. Chemical analysis of the raw materials (XRF).

Each frit was ground in an eccentric mill (500mL, alumina) with the addition of 10% kaolin, 0.2% sodium tripolyphosphate, 0.2% carboxymethylcellulose and 30% water, forming glaze slurries with a controlled density (1.80g/cm³) and viscosity (100s flowing time in Ford cup n° 4). The glazes were applied in layers of 0.4mm thickness over previously engobed tiles and fired in four thermal cycles: 900°C, 1,000°C, 1,100°C and 1,190°C for 40min in a laboratory roller kiln. The glaze colour was determined by spectrophotometry (d8 geometry, specular reflection, 400nm to 700nm, 10nm step). The microstructure was determined by x-ray diffraction (XRD CuKα, 0° to 75°, 0.02°/min) and scanning electron microscopy (SEM, 20kV) after etching the glaze samples with 5% (vol.) HF.

3. RESULTS AND DISCUSSION

3.1. Characterization of phases formed after firing:

Figure 1 shows the diffractograms for frits F1 to F4 used as ceramic glazes and fired at 1,100°C for 40 minutes. There is strong crystallization of all glazes,

with a smaller amount of glassy phase (baseline of the spectra). The main phases identified in frit F1 are titanite (sphene) and β quartz with rutile phase as a minor phase. For frit F2 the main phases are titanite and rutile. In frit F3 the main phases identified are titanite (sphene) and rutile, with quartz as minor phase. For F4, the main phase formed is also titanite, with formation of quartz and albite as minor phases. Figure 2 shows the diffractograms for all glazes derived from frits F1 to F4 and fired at 1,190°C for 40 minutes. For this temperature there is a decrease in the crystallization of all glazes, inferred by the reduction of peak height in relation to the treatment at 1,100°C, and an increasing amount of glassy phase, represented by the baseline of the spectra. The main phases identified in frit F1 (1,530°C/60min) are titanite (sphene) and rutile, with a large amount of glassy phase, according to the height of the baseline for the peaks of the main phases. For F2 (1,530°C/90min) only titanite was identified and there is an increase in the glassy phase. Frit F3 (1,480°C/60min) presents titanite (sphene) and rutile as main phases, with a large amount of glassy phase. Finally, for F4 frit (1,480°C/90min), the main phases formed were also titanite and quartz β, this being the glaze with the smallest amount of glassy phase. The amount of glassy phase was inferred from the comparison of the baseline of each frit in each treatment as a quantitative feature.
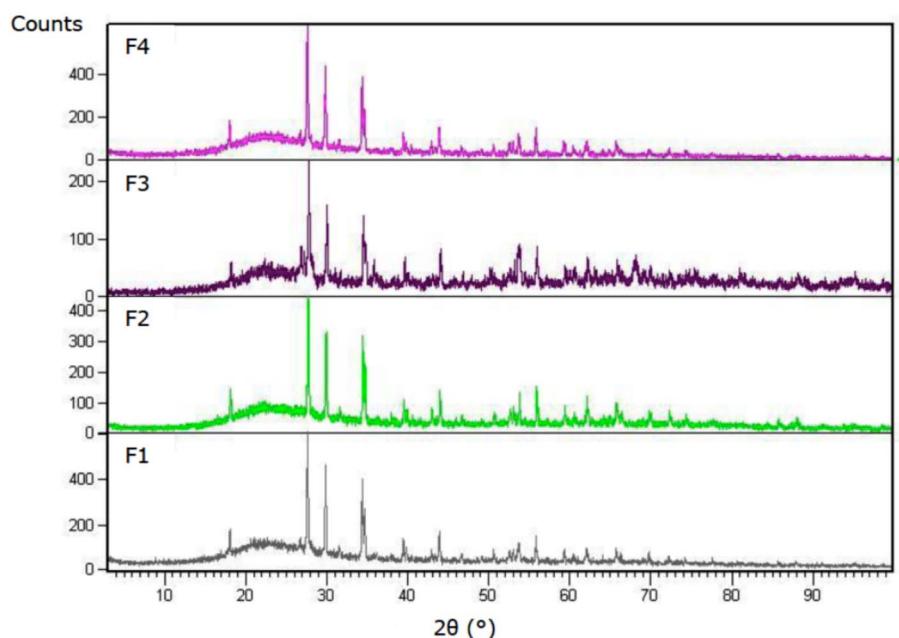

Figure 1. XRD patterns for frits F1 to F4 applied as glazes and fired at 1,100°C for 40 minutes.
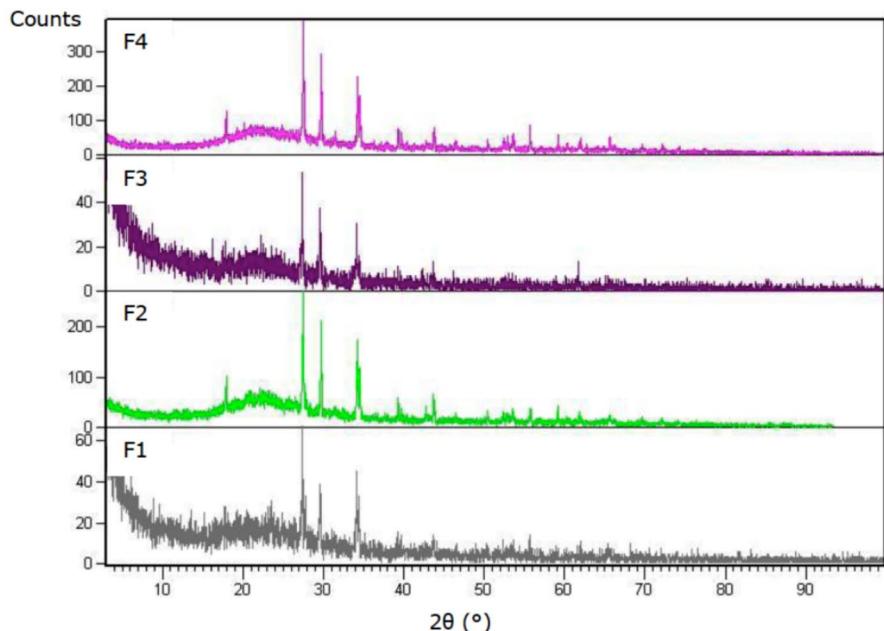
Figure 2. XRD patterns for frits F1 to F4 applied as glazes and fired at 1,190°C for 40 minutes.

3.2. Analysis of glaze opacity.

From the results in table 2, glaze F1 is more light than glazes F2 and F3, coordinate L*, and the luminosity difference for these glazes is above the limit of human visual acuity (ΔL*~0.50). Glazes F2 and F3 are the darkest of the four glazes studied for the temperature treatment of 1,100°C, but all values are close to the maximum luminosity value (L*=100), and all glazes are light. Regarding the a* coordinate, there is a tonality inversion into green (negative values of a*) in all glazes, with the lowest values obtained for glazes F2 and F3, less green and closer to the achromatic point for this tonality. The b* coordinates for all samples showed a lower tendency to yellow (+b*), and the lowest intensities occur for glazes F2 and F3.

Coordinate (Judd)	F1	F2	F3	F4
L*	95.61	95.01	95.00	95.34
a*	-0.77	-0.53	-0.56	-0.81
b*	3.61	3.36	3.35	3.6

Table 2. Chromatic coordinates for glazes F1 to F4 fired at 1,100°C.

3.3. Microstructural analysis of the glazes.

Figure 3 shows the microstructural evolution of the glaze made from frit F2, i.e., melted at 1,530°C for 90min. The firing of the F2 glaze from 1,000°C to 1,190°C evolves from a fully glassy phase, Figure 3a, through a glass-ceramic microstructure, with regular small crystals embedded in the glass matrix, Figures 5b and 5d, until a glass matrix structure again dominates, figure 3c.
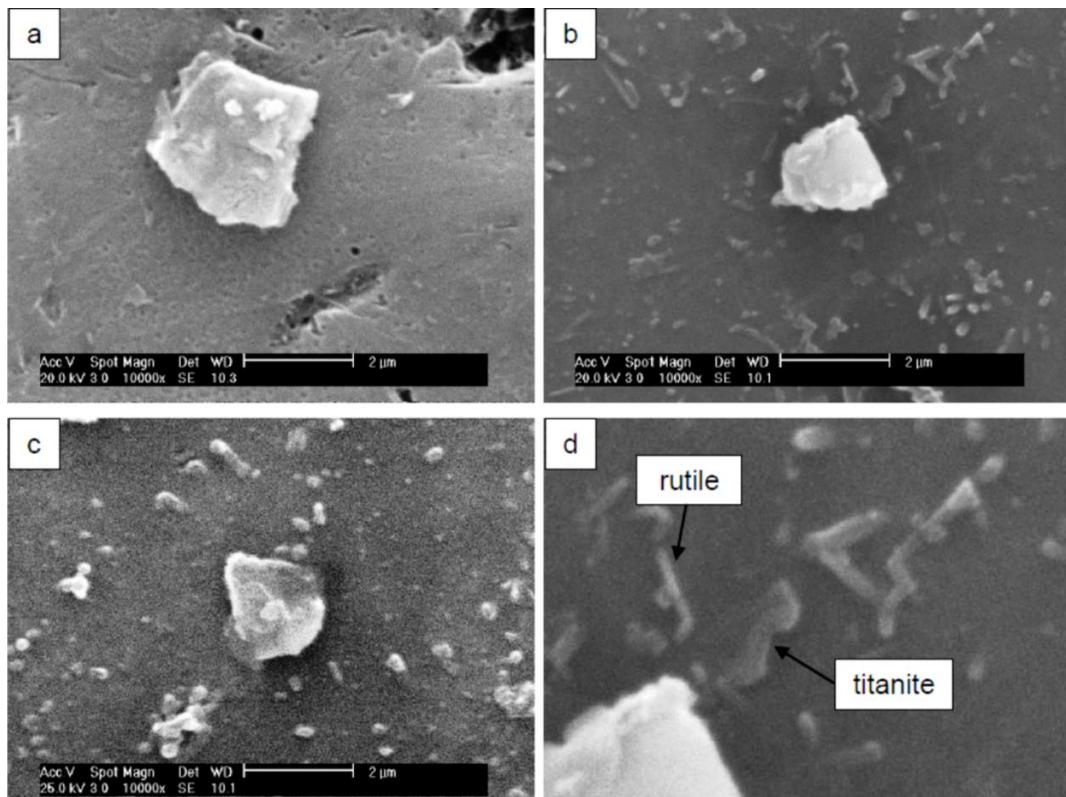
Figure 3. Microstructural evolution of frit F2 (1,530°C, 90min) glazed and fired at: (a) 1,000°C, (b) 1,100°C, and (c) 1,190°C; (d) detail of (b).

The microstructure shown in figure 3 is consistent with the results obtained by the X-ray diffraction technique, where at 1,000°C the microstructure of glaze F2 is almost glassy, with a few crystalline phases identified (mainly titanite, figure 2). At 1,100°C crystallization is intense, with the formation of titanite and rutile in F2 glaze (figure 1). At 1,190°C there is an increase in the glassy phase and again the titanite phase is predominant (figure 2). The small crystals identified in glaze F2 at 1,100°C, figures 5b and 5d, have nanometric dimensions and form acicular and rounded shapes. The needle-like forms are related to the rutile phase, and the more rounded with titanite or sphene (calcium titanate). The study by Teixeira and Bernardin [30] linked the yellow colour to the titanite phase, and white to the rutile phase, which may be associated with a high lightness of the glaze made from frit F2 when fired at 1,100°C, table 2.

4. CONCLUSION

The titanium oxide, widely used for metal enamelling, was replaced by zirconium oxide in ceramic glazing, because ZrO_2 has a higher stability of the white colour in a wide temperature range, but should be used in large amounts in frit melting [30]. However, the titanium oxide in anatase form has great capacity of opacification, and its tendency for yellowing depends on the temperature and time of frit melting and also the temperature and time of glaze firing, when the anatase frit is applied over ceramic substrates. The best results were obtained by adding 10% (mass

fraction) anatase to a calcium borosilicate frit, melted at 1,530°C for 90 minutes, and applied as a glaze and fired at 1,100°C in a 40 minute cycle. The whiteness of this frit is due to the formation of crystals of titanite (sphene) and rutile, but without the identification of the major fraction of each phase. Previous studies have shown that a white anatase frit with great covering capacity (opacification) was obtained by formation of rutile crystals from the glass matrix, and if titanite was formed then the frit presented yellowness [30]. In this study once more the main phases were identified as rutile and titanite, and the frit melted at 1,530°C for 90min presented rutile and titanite phases; however, as it appears white and opaque, the major phase is probably rutile.

REFERENCES

[1]   Kuchinski FA. En: Wachtman JB, Haber RK, editores. Ceramic films and coatings. Noyes Publications, 1993. p. 97-100.

[2]   Kinzie CJ, Plunkett JA. Titanium compounds and application thereof in vitreous enamels. Journal of the American Ceramic Society. 1935;18(1-12):177-122.

[3]   Yee TB, Andrews, AI. The relation of viscosity, nuclei formation, and crystal growth in titania-opacified enamel. Journal of the American Ceramic Society. 1956;39(5):188-195.

[4]   Fiedberg AL, Fischer RB, Petersen FA. Effect of size and shape of titanium oxide crystals on spectrophotometric properties of titanium-bearing porcelain enamels. Journal of the American Ceramic Society. 1948;31(9):246-253.

[5]   Engel WH, Eppler RA, Parsons, DW. Transmission electron microscopy of TiO_2 opacified porcelain enamels. American Ceramic Society Bulletin. 1970;49(2):175-179.

[6]   Eppler RA. Microstructure of titania-opacified porcelain enamels. Journal of the American Ceramic Society. 1971;54(12):595-600.

[7]   Olympia FD. Ceramic Bulletin. 1953;32(12):412-414.

[8]   Eppler RA, McLeran Jr WA. Kinetics of opacification of a TiO_2-opacified cover coat enamel. Journal of the American Ceramic Society. 1976;50(3):152-156.

[9]   Eppler RA. Crystallization and phase transformation in TiO_2-opacified porcelain enamels: Theory. Journal of the American Ceramic Society. 1969;52(2):89-94.

[10]   Eppler RA. Crystallization and phase transformation in TiO_2-opacified porcelain enamels: Comparison of theory with experiment. Journal of the American Ceramic Society. 1969;52(2):94-99.

[11]   Teixeira S, Frajndlich EUC, Riella HG, Bernardin AM. Development of TiO2 white glazes for ceramic tiles. En: X Congreso Mundial de la Calidad del Azulejo y del Pavimento Cerámico. Castellón: Official Chamber of Commerce, Industry and Navigation, v.1, 2008. p.115-122.

[12]   Teixeira S, Bernardin, AM. Development of TiO_2 white glazes for ceramic tiles. Dyes and Pigments. 2009;80:292-296.