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Development of TiO_2 white glazes for ceramic tiles☆

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ABSTRACT

The objective of this work was the use of titania polymorphs (rutile and anatase) in substitution of zirconia as the main component for producing white opacity in ceramic glazes for tile coatings. Initially, total zirconia (12% mass fraction) was replaced in the standard frit by rutile and by anatase in mass fractions of 5%, 10% and 15%, forming two frit groups processed as ceramic glazes. The glaze color was determined by spectrophotometry and the glaze microstructure by XRD and SEM. The results showed the frit containing 10% anatase formed a totally white glaze presenting excellent coating capacity. The frits containing rutile produced yellow opacity. The results of microscopy and X-rays diffraction revealed that opacity was caused by tiny rutile crystals in the anatase frits and by titanite crystals in the rutile frits.

1. Introduction

White and opaque glaze coatings are used in the ceramic tile industry to form a base on which layers of serigraphy can be applied. Traditionally, industrial glazes for ceramic tiles use zircon or zirconia as opacity agents for coating, the former is 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.

In the 19th century, titanium compounds were known fluxes for porcelain glazes and crystallites of TiO_2 formed during firing generated opacity; however, they did not yield white coatings [1]. Impurities (Fe, Cr, etc.) present in the raw materials produced non-white coats until more pure forms of TiO_2 became available [2]. Some studies reported the relationship between TiO_2 crystallite size and shape and the resulting reflectance and color, identifying rutile and anatase phases, with the acicular rutile particles occurring at higher temperatures or longer firing times and the rounded anatase particles forming earlier in the firing process [3]. Blue color was associated with the smaller rounded anatase particles and yellow color, formed at the later stages of firing, was associated with the dissolution of the anatase particles at the expense of the larger rutile particles. The color change (blue to yellow) corresponds to a large increase in the rutile/anatase ratio [3].

SEM studies confirmed that rutile crystals were always present with an acicular morphology, however, anatase crystals were observed with cubic, rectangular and acicular morphologies [4]. Additionally, anatase nucleation is a bulk phenomena and rutile nucleation occurs at the interface between adjacent frit particles [5]. The depletion of anatase crystallites near rutile surface crystals indicates that the anatase to rutile inversion is a ripening process as opposed to a phase transformation. Nucleation (at 425–460 °C) and growth rates (at 620–720 °C) control the resultant crystal phases and morphologies [6]. Moreover, temperature exhibits a greater effect than time on glass viscosity and growth rates for TiO_2-opacified enamels [2]. The thermal history of porcelain enamel has a major effect, two- or three-fold, on the measured viscosity. Thus, the consistency of the smelting and quenching process for the manufacture of TiO_2-opacified frits are even more important than for many other porcelain enamels and glazes.

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 color data did not correlate well with the observed, or predicted,

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Table 1
Compositional formulas for the studied frits (TiO_2 for rutile and anatase frits)

Formula	Standard	5%	10%	15%
SiO_2	62.3	63.1	60.7	56.3
Al_2O_3	4.7	5.0	4.7	4.3
CaO	7.4	7.9	8.2	7.2
Na_2O	13.2	4.8	5.1	4.9
K_2O	0.6	0.1	0.5	0.4
ZrO_2	12.0	–	–	–
TiO_2	–	5.0	10.0	15.0
MgO	1.4	0.0	1.4	0.0
Fe_2O_3	0.8	0.1	0.1	0.1
B_2O_3	4.8	5.2	4.9	4.7

crystalline concentration data [8,9]. Regarding the physical properties of porcelain glaze (like viscosity) for resultant reflectance and color, porcelain glazes produce reflectance via opacifiers, including crystallites (such as TiO_2 or ZrO_2), but may also include insoluble materials, phase separated glasses and gas bubbles. The factors that control the opacity in porcelain glazes are refraction index difference between the glass and opacifier; glass and opacifier absorption; the size and shape of the opacifier; opacifier distribution; number of particles; incident light wavelength; and porcelain glaze (or enamel) thickness [10].

High refraction indices for TiO_2 (rutile: 2.76 and anatase: 2.52) compared to that of typical porcelain glazes (1.50–1.55) make TiO_2 the best selection for opacification of glazed ceramics [10]. Other typical opacifiers, SnO_2 (2.04), Sb_2O_3 (2.09) and ZrO_2 (2.17) are not as effective as TiO_2. Numerous compositional effects exist on TiO_2-opacified porcelain glazes [10,11]. Na_2O is preferable to K_2O for flow, color and reflectance, with K_2O causing a decrease in viscosity, resulting in more anatase crystals and a bluish-white color. K^+ has been used to stabilize the anatase phase in pigment research [12]. P_2O_5 enhances the blueness of porcelain glazes through an acceleration of anatase formation relative to rutile. Both crystals exhibit enhanced nucleation rates, but anatase is accelerated by twice that of rutile; thus, PO_4^{3-} is used to stabilize the anatase structure [12–14]. Sb and Nb additions enhance the blueness of titania-opacified glazes, probably because these elements retard crystal growth, producing a coating with smaller crystals and a large number of anatase crystals [15]. A reduction in viscosity and improvement in acid resistance are other beneficial effects of TiO_2 additions to porcelain glazes and enamels [16]. TiO_2 was shown to decrease the viscosity of all porcelain glazes except those with high (>20%) P_2O_5 compositions. Only additions of <11% TiO_2 reduce the viscosity and greater amounts increase it [17,18].

In addition to time/temperature relationships and compositional effects, numerous other factors can effect crystallization and resultant reflectance and color of porcelain glaze coatings. Two other major influences are mill additions and furnace atmosphere conditions. Mill additions can directly influence porcelain glaze viscosity and oxidation/reduction conditions in the coating. Both these effects alter the fired coating [19,20]. The furnace atmosphere also alters the oxidation/reduction conditions and can alter glass viscosity through moisture variations. All these process variables lead to tight controls on production conditions and specialized development of coating systems for most glazing plants on an individual basis.

Some studies [21–24] have shown that compositions based on the titanite system ($CaO \cdot TiO_2 \cdot SiO_2$) tend to generate opaque white glazes. Titanite crystals devitrify from the frit in the glaze composition during tile firing [22,23], 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 coloring applications [25].

2. Experimental procedure

Initially, total zirconia (12% mass fraction) was replaced in the standard frit by rutile and by anatase in mass fractions of 5%, 10% and 15%, forming two frit groups (Table 1). The frits were melted at 1450 °C and quenched in water. Each frit was ground in an eccentric mill with the addition of 10% of kaolin, 0.2% of sodium tripolyphosphate, 0.2% of carboxymethylcellulose and 30% of water, forming glaze slurries with a controlled density (1.80 g/cm^3) and viscosity (50 s flowing time in Ford cup no. 4). The glazes were applied in layers of 0.4 mm thickness over previously engobed tiles and fired in two thermal cycles: 1117 °C for 22 min and 1130 °C for 27 min, both in a roller kiln ("monoporous" fast firing heat treatment). The glaze color was determined by spectrophotometry (*d*8 geometry, specular reflection, 400–700 nm, 10 nm step). The microstructure was determined by X-ray diffraction (XRD Cu Kα, 0–75°, 0.02°/min) and scanning electron microscopy (SEM, 20 kV).

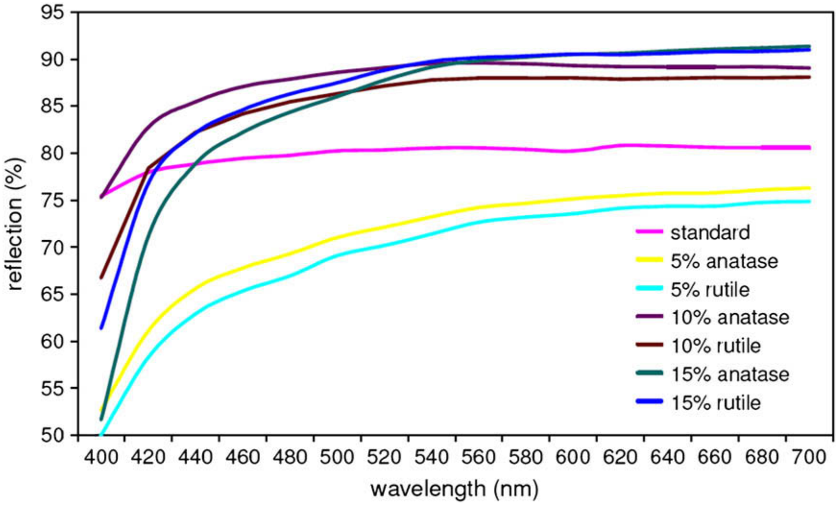

Fig. 1. Reflectance spectra for 5%, 10% and 15% anatase and rutile glazes fired under the 1117 °C/22 min cycle.

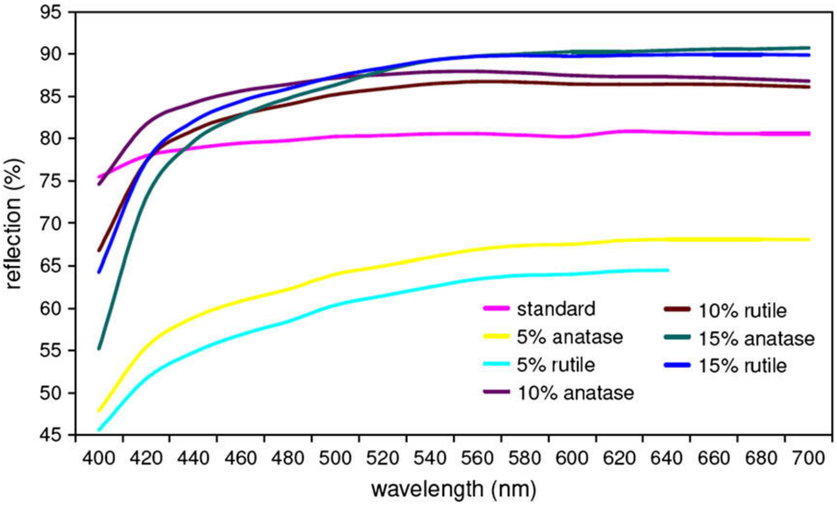

Fig. 2. Reflectance spectra for 5%, 10% and 15% anatase and rutile glazes fired under the 1130 °C/27 min cycle.

3. Results and discussion

Under the 1117 °C/22 min cycle, both glazes (anatase and rutile) presented a yellowish coating, but under the 1130 °C/27 min cycle the yellow appearance diminishes for both glazes, showing the influence of temperature and time on crystal formation and glaze opacity. At 10% anatase and rutile addition, the yellow tonality diminishes for both glazes at 1117 °C/22 min. Both glazes present a strong covering effect compared to the standard zirconia glaze. Under the 1130 °C/27 min cycle, the anatase glaze is visually whiter than the standard zirconia glaze. Finally, at 15% titania addition, a complete coating is obtained for both glazes at both firing cycles (1117 °C/22 min and 1130 °C/27 min) compared to the zirconia standard; however, at this point both glazes again appear yellowish.

Under the 1117 °C/22 min cycle, all glazes were more opaque than the standard, except for 5% anatase and rutile addition (Fig. 1). The reflectance for 10% and 15% anatase and rutile glazes was greater than the standard reflectance, beginning at 420 nm, demonstrating the more effective covering effect of these glazes. However, the reflectance of these glazes diminished at violet and blue wavelengths (400–500 nm) and increase at longer yellow and red wavelengths (600–700 nm), justifying the yellowish tonality of these glazes.

At 1130 °C/27 min, again the 5% anatase and rutile glazes presented a lower covering effect than the zirconia standard glaze (Fig. 2). The 10% and 15% glazes (anatase and rutile) were more opaque than the standard, with higher reflectance in comparison with the zirconia glaze. The anatase glaze presented a straighter curve for all wavelengths, mainly in the violet and blue regions (400–500 nm), explaining its whiter behavior in relation to the standard glaze (Fig. 2).

Since the opacity of white glazes is obtained by crystallization of the glass system, the yellow or white opacity of titania glazes is explained by the phases developed during glaze heat treatment. Fig. 3 shows the XRD results of the standard glaze in comparison with the 5% anatase and rutile glazes for both firing cycles (1117 °C/22 min and 1130 °C/27 min). At 1117 °C/22 min, the standard glaze was the only one that presented well-developed crystalline phases; the glazes containing 5% anatase and rutile additions did not present well-defined crystalline phases, justifying the poor covering properties shown by their reflectance curves. No crystalline phases have developed in the 5% anatase glaze under the 117 °C/22 min cycle, however, titanite (calcium titanium silicate)

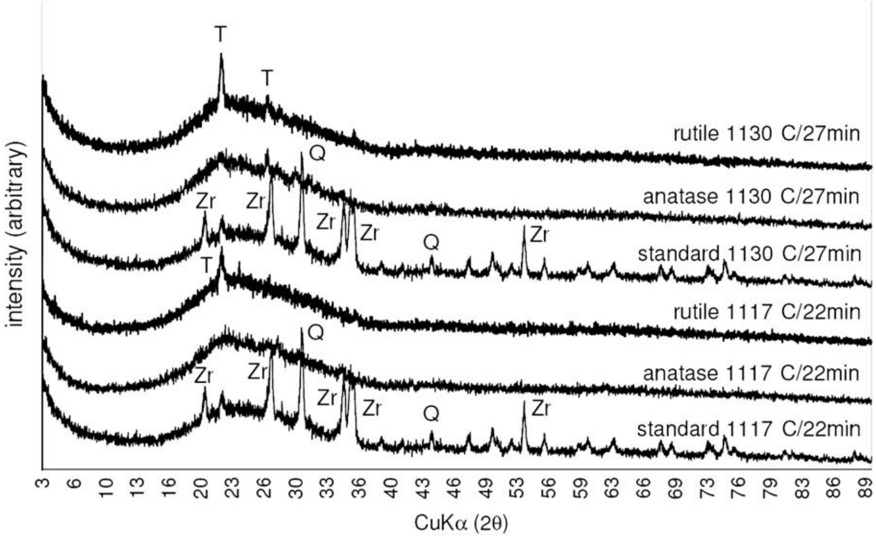

Fig. 3. XRD patterns for 5% TiO_2 addition (anatase and rutile glazes) under the 1117 °C/22 min and 1130 °C/27 min firing cycles (Q = quartz; T = titanite; Zr = zircon).

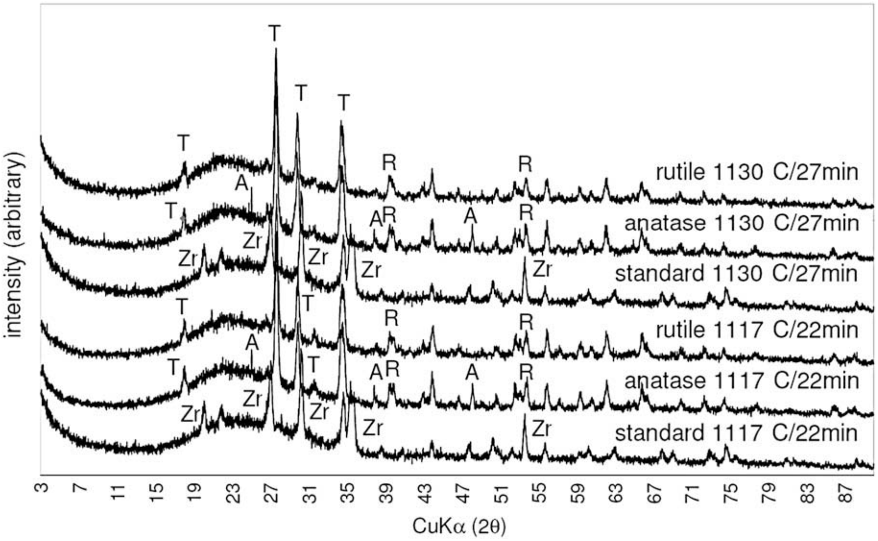

Fig. 4. XRD patterns for 10% TiO_2 addition (anatase and rutile glazes) under the 1117 °C/22 min and 1130 °C/27 min firing cycles (A = anatase; Q = quartz; T = titanite; Zr = zircon).

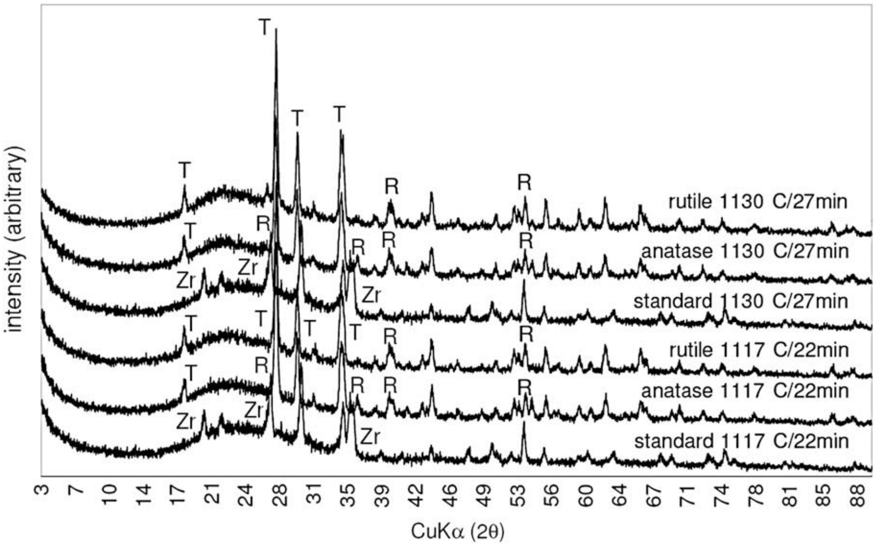

Fig. 5. XRD patterns for 15% TiO_2 addition (anatase and rutile glazes) under the 1117 °C/22 min and 1130 °C/27 min firing cycles (R = rutile; T = titanite; Zr = zircon).

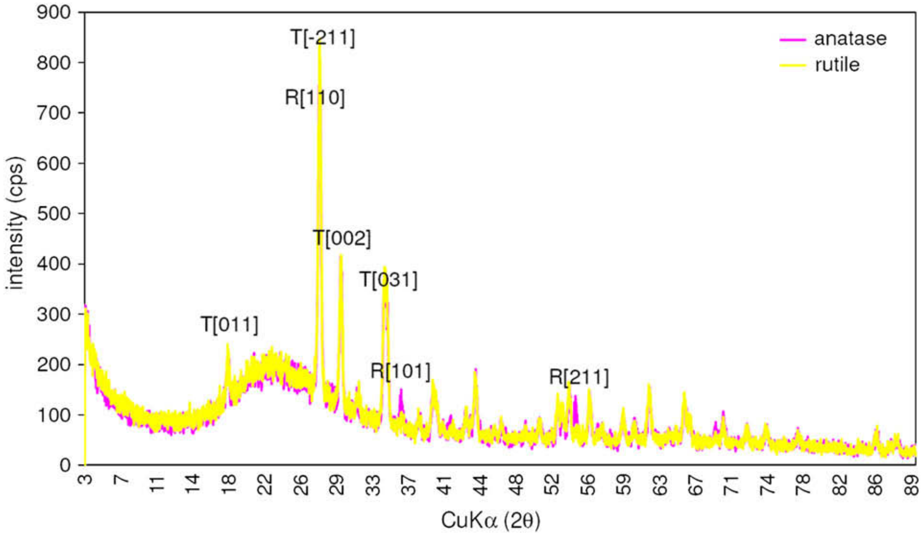

Fig. 6. XRD patterns for 15% TiO_2 addition (anatase and rutile glazes) under 1130 °C/27 min firing cycle (R = rutile; T = titanite).

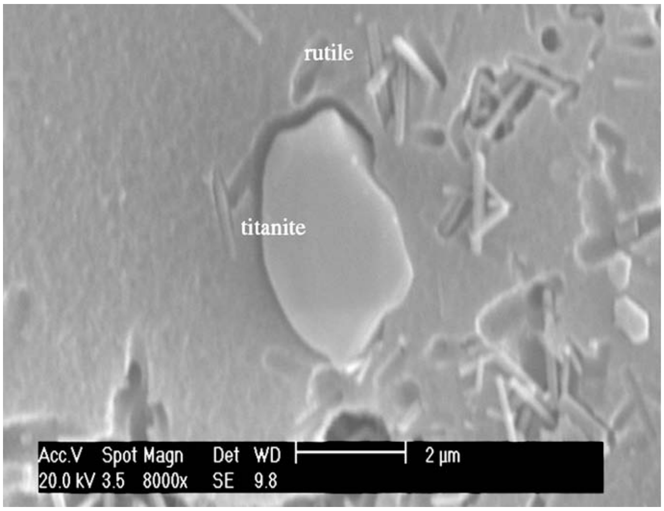

Fig. 7. SEM microstructure of the rutile glaze fired at 1117 °C/20 min.

developed in the rutile glaze. At 1130 °C/27 min, α quartz presented greater crystallization in the anatase glaze and titanite in the rutile glaze.

The XRD results for the 10% anatase and rutile glazes are shown in Fig. 4. At 1117 °C/22 min, the rutile glaze developed titanite (main peaks (2θ:[*hkl*]): 17.93:[011], 27.48:[−211], 29.76:[002] and 34.27:[031]) [26] and rutile (main peaks (2θ:[*hkl*]): 27.50:[110], 36.17:[101] and 54.46:[211]) [27] phases and showed no α quartz phase; the anatase glaze developed titanite and anatase (main peaks (2θ:[*hkl*]): 25.33:[101], 37.82:[004] and 48.09:[200]) [28], with reduced α quartz. At 1130 °C/27 min, the anatase phase remained in the anatase glaze, with some rutile and titanite; titanite is more developed in the rutile glaze (peak height), which explains the yellowish color of the rutile glaze.

The XRD results for the 15% anatase and rutile glazes are shown in Fig. 5. At 1117 °C/22 min, the rutile glaze developed mainly titanite (with some rutile) and the anatase glaze developed both titanite (less intense peaks) and rutile. Both glazes presented well-developed crystalline phases, even when compared to the standard zircon glaze. At 1130 °C/27 min, the anatase phase completely disappeared from both glazes, becoming a transitory phase. The rutile glaze presented titanite; the anatase glaze presented both titanite and rutile and, again, the yellowish aspect. The difference between the rutile and anatase glazes is that the rutile glaze presents more developed titanite phase (peak height), and the anatase glaze presents more developed rutile phase, Fig. 6.

Finally, Fig. 7 shows the microstructure of the 15% rutile glaze fired at 1117 °C/20 min. The round particle is titanite and the needle like particles are rutile.

4. Conclusion

The presence of TiO_2 in ceramic glazes causes the onset of their crystallization, because TiO_2 is the first oxide system to precipitate in the liquid glass; thus, it acts as a nucleating agent, forming rutile and anatase when in a pure form, and other phases, such as quartz and titanite. Apparently anatase is the most efficient nucleating agent: at the onset, the anatase frit formed anatase at low temperatures; at higher temperatures the anatase phase transformed into rutile and possibly directly to titanite. The rutile frit formed titanite directly; the crystalline phase that results in the yellow appearance of titania glazes. So the use of titanium oxide in the anatase form is very efficient for obtaining white glazes and a 10% addition resulted in great opacity, better than the zircon glaze used in this study.

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