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Titania slag as a ceramic pigment

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Abstract

The phase transformations and colouring mechanisms that occur during the ceramic processing of titania slag were investigated using XRF-EDS, XRD, DRS and laboratory-scale application in glazed and unglazed tiles. The slag transforms to pseudobrookite, undergoing a drastic colour change during firing as a consequence of thermal oxidation with Fe^{2+} to Fe^{3+} and Ti^{3+} to Ti^{4+} reactions. The intense brown colour imparted by titania slag is stable at both low (up to 1050 °C) and high (around 1200 °C) temperatures and is suitable for porcelain stoneware tiles. In through-body application, titania slag enables 'spotting' effects to be achieved.

Keywords: Ceramic pigment; Optical properties; Pseudobrookite; Titania slag

1. Introduction

Titania slag is an important Ti ore, with a world output around two million of cubic tons per year [1]. It is obtained by smelting a mixture of ilmenite ($FeTiO_3$) and rutile (TiO_2) in order to enrich the Ti content of ilmenite (the most abundant titanium ore) and to improve the yield of successive processing steps [2–4]; the slag is used in the TiO_2 production by either hydrosulphuric acid dissolution [5,6] or chlorination [7].

The smelting process is carried out at temperatures around 1600 °C in a strongly reducing atmosphere, ensured by adding coal to Ti ores [2–4]. The slag, obtained by decrepitation [8], is to a large extent vitreous. The main crystalline phase is typically pseudobrookite, with minor residual rutile and ilmenite [9–11]. Pseudobrookite is a solid solution of $Fe^{2+}Ti_2^{4+}O_5$, $Ti^{4+}Ti_2^{3+}O_5$ and $Ti^{4+}Fe_2^{3+}O_5$ end terms, implying the occurrence of multiple valences of iron and titanium [9,10,12,13]. Its stoichiometric composition is M_3O_5 which is consistent with the compositional invariance observed in titania slags [14]. However, it has been shown that pseudobrookite appears as the main crystalline phase only when reduction of ilmenite is carried out at temperatures above 1200 °C while rutile and ilmenite are the prevailing phases at temperatures below [15].

Titania slag easily undergoes thermal oxidation, involving Fe^{2+} to Fe^{3+} and Ti^{3+} to Ti^{4+} reactions [16,17]. Oxidation phenomena may occur even at low temperature [18] and are promoted by water vapour [17].

Although titania slag has been occasionally used in the latest years in the manufacturing of ceramic tiles to get low cost brown colours, no information is available in the literature on this new application. Therefore, the present study is aimed at understanding phase transformations, colouring mechanisms and technological behaviour of titania slag, used as a ceramic pigment in the tile-making process.

2. Experimental

A commercial titania slag, currently used in the ceramic tile industry, was sampled in the form of rounded grains below 1 mm and characterized from the following viewpoints:

- chemical composition by X-ray fluorescence energy dispersive spectrometry (XRF-EDS, Link Analytical microprobe eLXI, 15 kV and 1 nA) as an average of three sub-samples;

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- mineralogical composition by X-ray powder diffraction (XRPD, Bruker D8 Advance equipped with solid state detector, Cu $K\alpha_{1,2}$ radiation, 10–100° 2θ, 0.02° step-scan, 13 s per step);
- optical properties by diffuse reflectance spectroscopy (DRS, Perkin Elmer λ35 spectrophotometer, 300–1100 nm range, 0.03 nm step-scan, $BaSO_4$ integrating sphere and white reference material); reflectance (R_∞) was converted to absorbance (K/S) by the Kubelka–Munk equation: $K/S = (1 - R_\mu)^2 \cdot (2R_\mu)^{-1}$.

Titania slag was tested as ceramic pigment in several glazes, glassy coatings and bodies currently used in the tile-making industry. For this purpose, it was dry ground in agate mortar down to a particle mean diameter of 12 μm (80 wt.% is in-between 1 and 30 μm). This pulverized slag was added (5 wt.%) to different glassy coatings (F1–F4) and glazes (S1–S4). Furthermore, it was introduced (1 wt.%) in porcelain stoneware bodies (B1 and B2) either in pulverized form or as-received grains. The chemical and physical characteristics of these ceramic matrices are reported elsewhere [19,20]. These tiles were fast fired in an electric roller kiln in industrial-like conditions and characterized by DRS and XRD. The technological potential of titania slag was assessed by comparing its colouring performance in ceramic applications with high-quality, brown and reddish pigments used by the tile-making industry [21,22]: $(Ti,Cr,W)O_2$ *tobacco* rutile (*abr.* RT), $(Fe,Zn)(Cr,Fe,Al)_2O_4$ *tan* spinel (ST), Fe_2O_3 *maroon* hematite (HM), $(Cr,Fe)_2O_3$ *dark brown* eskolaite (EB), and Fe_2O_3–$ZrSiO_4$ *coral* zircon (ZC).

3. Results and discussion

3.1. Characteristics of titania slag

The titania slag utilized in the tile-making industry contains approximately 62% TiO_2 and 32% FeO, with Si, Al, and Mn as main impurities (Table 1). Thus it is classified as low-Ti slag with a Fe–Ti ratio close to the $Fe_{0.32}Ti_{0.68}$ eutectics along the $FeO\cdot Fe_2O_3$–TiO_2 join [12, 23].

Table 1
Chemical composition of titania slag

	Average (wt.%)	Standard deviation
TiO_2	64.46	0.84
FeO_{tot}	30.49	0.72
SiO_2	1.74	0.23
Al_2O_3	1.43	0.11
MnO	1.06	0.15
CaO	0.33	0.09
MgO	0.30	0.02
V_2O_5	<0.3	
CoO	<0.2	
Cr_2O_3	<0.1	
Total	99.80	

Ilmenite and rutile are the main crystalline compounds found in the titania slag under investigation; a minor amount of anatase is also present. The occurrence of a remarkable amount of glassy phase is denoted by the high background and particularly by the characteristic hump in the 20–40° 2θ range of the diffraction pattern (Fig. 1). A rough estimate of relative proportions of the crystalline phases, neglecting the abundant amorphous component, is 43% ilmenite, 47% rutile, 10% anatase. All these crystalline phases exhibit a very low degree of structural order, inferred by their very broad lines that do not permit any reliable determination of unit cell dimensions. It is likely that ilmenite and a small fraction of rutile are relics of primary ores, while most of the rutile has been produced during the ilmenite reduction. Furthermore, very little information can be gained on the short range order of the amorphous phase which might resemble the one expected for pseudobrookite-like structures with M_3O_5 stoichiometry. The absence of well developed crystalline pseudobrookite phases may be explained by a relatively lower than usual temperature of processing achieved by the titania slag material under study [15].

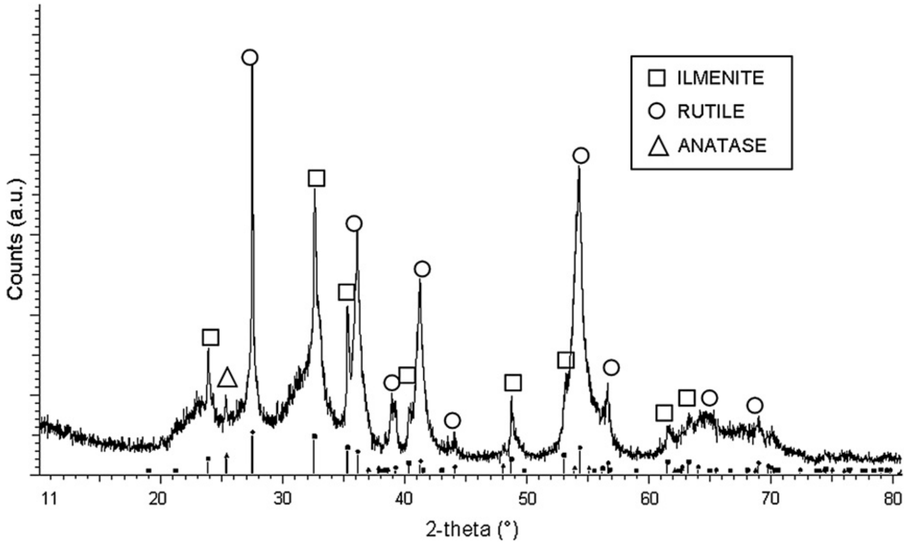

Fig. 1. XRD pattern of titania slag showing the presence of ilmenite, rutile and anatase.

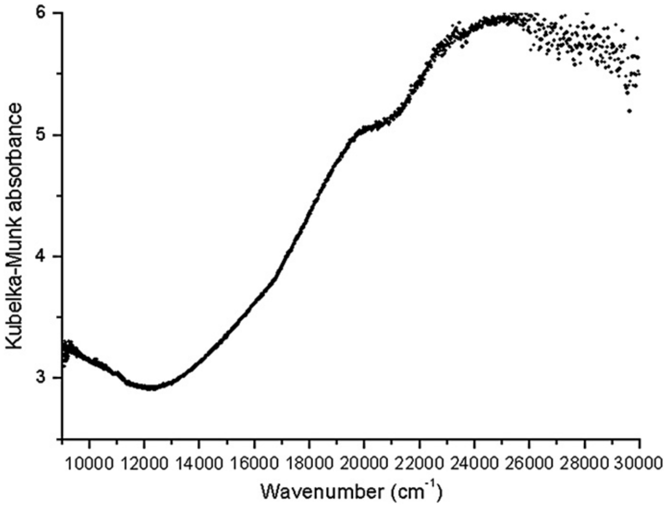

Fig. 2. Diffuse reflectance spectrum of titania slag.

The main optical feature of titania slag is the intense light absorption all over the spectrum, with a maximum reflectance in the 11 000–15 500 cm^{-1} range, that justifies its dark colour with a reddish cast (Fig. 2). This strong absorbance is due to both d–d electron transitions and charge transfer phenomena [24,25], particularly the $^5T_{2g}$ (^5D) → ^5E_g (^5D) transition of octahedrally coordinated Fe^{2+} in ilmenite, that is able to explain the light absorption below 12 000 cm^{-1}, and the $^2T_{2g}$ (^2D) → ^2E_g (^2D) transition of Ti^{3+} in sixfold coordination, in defective rutile and/or ilmenite, to which the bands in the 15 000–22 000 cm^{-1} range may be attributed. Moreover, a Ti^{3+} → Ti^{4+} intervalence charge transfer (IVCT) may occur in both ilmenite and rutile, accounting for the intense band at ~20 000 cm^{-1}, and a metal–ligand charge transfer (MLCT), like Fe–O and/or Ti–O, is responsible for the absorbance at high energies, peaking at ~25 000 cm^{-1}.

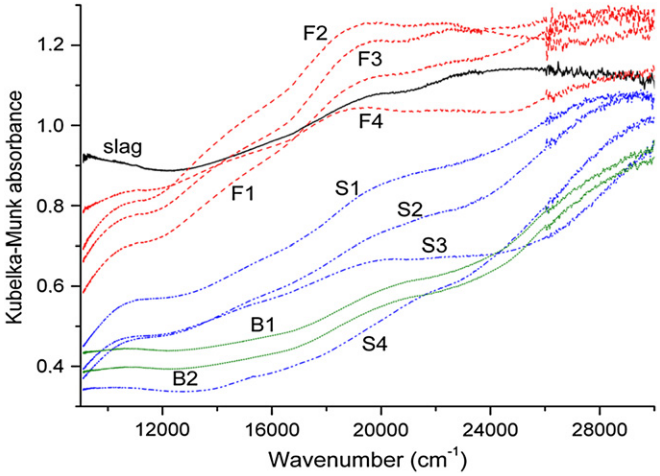

Fig. 3. Diffuse reflectance spectra of slag-bearing glassy coatings (F1–F4), glazes (S1–S4) and porcelain stoneware bodies (B1 and B2).

This picture confirms that most of the iron and titanium is in the reduced form (Fe^{2+} and Ti^{3+} [9,10]) even if a significant amount of Fe^{3+} and Ti^{4+} cannot be ruled out on the basis of optical spectroscopy.

3.2. Colouring mechanism

Titania slag undergoes a drastic colour virage once applied in ceramic matrices, that essentially consists in a slope change in the optical spectra (Fig. 3). This implies a decreased absorbance at low energies (9000–18 000 cm^{-1}) that roughly corresponds to an increased emission of red to yellow wavelengths, so explaining the brown coloration bestowed on ceramic wares. However, the spectral features are quite similar in every ceramic matrix, the main difference being the light

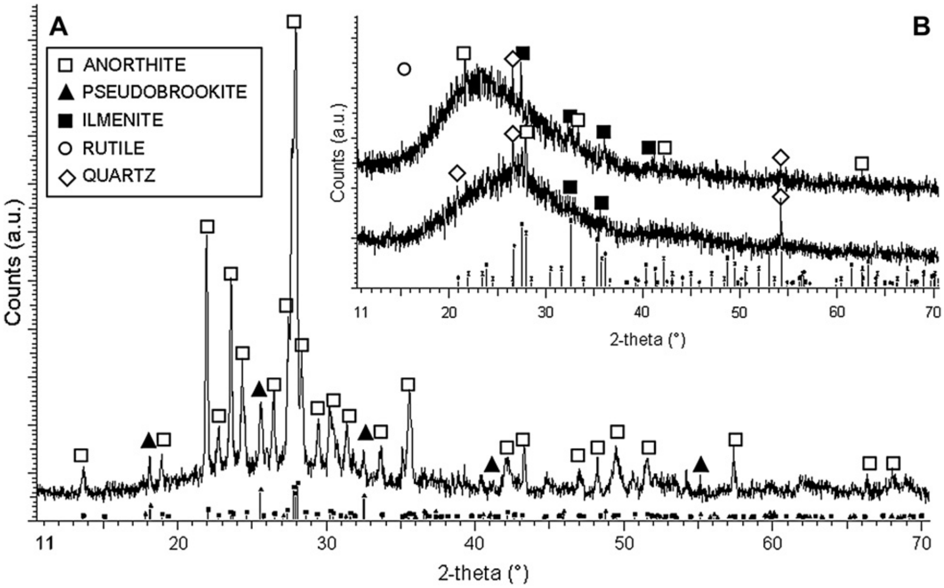

Fig. 4. XRD patterns of (A) the floor tile glaze S1 and (B) the wall tile glassy coating F1 containing titania slag.

absorbance, decreasing from glassy coatings to glazes and down to porcelain stoneware bodies (Fig. 3).

This colour change is connected with phase transformations occurring to titania slag during the firing process of ceramics. The XRD patterns of glassy coatings (Fig. 4) fired at 750 °C (F4) and 1000 °C (F1) show that the fraction of crystalline phases in these samples is negligible. This can be due either to a dilution effect or to dissolution of the crystalline phases belonging to the titania slag. On the contrary, the XRD pattern of the floor tile glaze fired at 1200 °C (S1) shows the occurrence of abundant anorthite (from the ceramic matrix) together with pseudobrookite (Fig. 4). This suggests that a significant recrystallization of both crystalline and amorphous phases from the slag has occurred.

Optical spectroscopy shows the disappearance of absorption bands attributable to Ti^{3+} and Fe^{2+}, that are replaced by others, referable to Fe^{3+} in octahedral coordination, hence probably hosted into the pseudobrookite structure [24,25]. Such bands are the Fe^{3+} d–d transitions from the ground state $^6A_1$ (^6S) to $^4T_1$, $^4T_2$ and $^4E + {}^4A$ (^4G) as well as to $^4T_2$ and ^4E (^4D), shown in Fig. 5A and 5B. A paired transition is present at $\sim 19\,000\ cm^{-1}$, due to magnetically coupled Fe^{3+} ions located in adjacent sites, even if a possible contribution from the $Ti^{3+} \rightarrow Ti^{4+}$ IVCT cannot be ruled out. Furthermore, there are optical effects related to $Fe^{2+} \rightarrow Fe^{3+}$ IVCT, accounting for the weak absorption at the red-IR border, and both Fe–O and Ti–O MLCT at high energy.

This optical pattern is clearly the consequence of thermal oxidation involving especially pseudobrookite, which is likely to transform from a $Fe^{2+}Ti^{4+}_2O_5$–$Ti^{4+}Ti^{3+}_2O_5$ solid solution toward a composition close to the $Ti^{4+}Fe^{3+}_2O_5$ end term. As a matter of fact, the spectra of titania slag-added glazes are quite similar to that of synthetic pseudobrookite [26], besides some difference is appreciable particularly at low wavenumbers (Fig. 5C). It may be attributed to the occurrence in titania slag of more pronounced intervalence effects, such as $Ti^{3+} \rightarrow Ti^{4+}$ and $Fe^{2+} \rightarrow Fe^{3+}$ at about 19 000 and 13 500 cm^{-1}, respectively.

3.3. Colouring performance

The changes in the optical spectra have repercussions on colour saturation – that fastly decreases from chocolate brown (*e.g.* glassy coating F2) to light maroon (*e.g.* glaze S1) to beige (*e.g.* body B1) – and on the a^* and b^* colourimetric parameters (Table 2).

Titania slag has a suitable behaviour in both low temperature (glassy coatings fired in the 800–1050 °C range) and high temperature applications (porcelain stoneware glaze S1, fired at 1200 °C). Its colour performance is deteriorated once temperatures over 1200 °C or very aggressive matrices (as the Ca- and Zn-rich glazes S2 and S3) are used. At all events, this is a common behaviour of ceramic pigments and especially of brown colorants, as it can be observed in Fig. 6, where the variation of CIE L^*, a^* and b^* parameters are plotted versus the firing temperature.

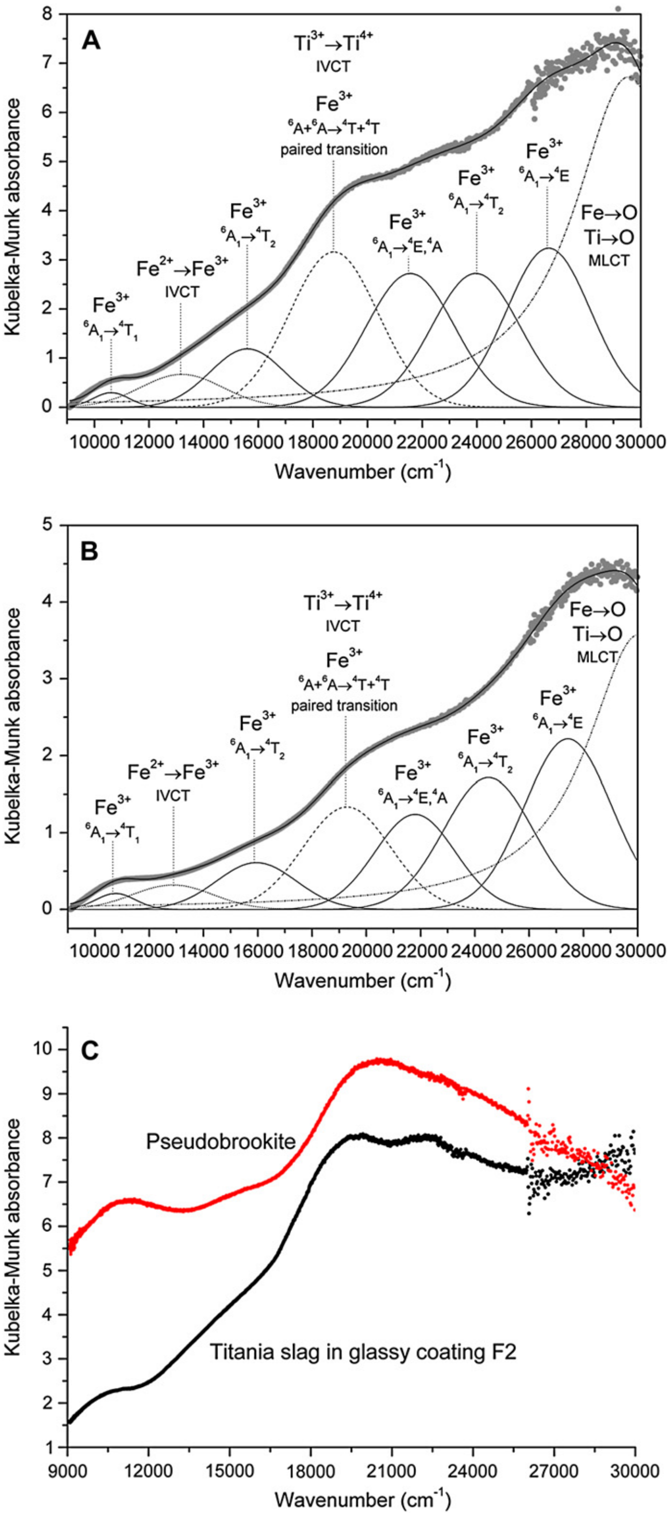

Fig. 5. Diffuse reflectance spectra of (A) the glassy coating F2 and (B) the glaze S1, both containing titania slag, with deconvolution of the main optical bands. (C) Comparison with optical spectrum of pure pseudobrookite [26].

Ceramic coatings containing titania slag exhibit a noteworthy increase of brightness (L^* values) for growing temperatures; however, this trend is superimposed to those of industrial pigments, that all suffer the same loss of colour saturation, but for the dark brown EB (Fig. 6). On the other hand, titania slag

Table 2
CIE $L^*a^*b^*$ parameters of ceramic matrices coloured with titania slag

Ceramic	Matrix	Application	Firing temperature (°C)	CIE lab parameters		
				L^*	a^*	b^*
Glassy coatings	F4	Third fire	750	39.32	3.31	3.96
	F3	Third fire	900	37.08	7.63	10.22
	F2	Wall tiles	950	33.26	6.62	6.53
	F1	Wall tiles	1000	38.90	6.50	10.21
Glazes	S3	Wall tiles	1100	58.12	3.86	6.73
	S2	Floor tiles	1150	55.66	3.05	13.01
	S1	Floor tiles	1200	50.16	5.55	13.03
	S4	Sanitaryware	1250	70.51	1.82	15.22
Porcelain stoneware bodies	B1	Floor tiles	1200	64.98	3.29	12.27
	B2	Floor tiles	1200	63.07	2.98	11.97

undergoes limited chromatic changes with increasing temperature, represented by a slight decreasing of the red component (a^*) and a more pronounced increasing of the yellow one (b^*) implying a colour virage toward an orange brown. At all events, similar trends are shown by RT, HM and ZC industrial pigments too (Fig. 6).

Unglazed floor tiles (porcelain stoneware) are usually coloured by through-body application involving pigment mixing together with raw materials [21,22]. Once applied in the pulverized form, titania slag gave rise to a pale brown coloration (Table 2). In contrast, it is able, when added in grains <1 mm, to impart an aesthetic ‘spotting’ effect that is endeavoured to reproduce some features of natural stones [22].

4. Conclusions

Titania slag is currently used like a pigment in the manufacturing of ceramic tiles to get low cost brown colours. Its colouring mechanism is due to changes in valences of transition metals hosted in the crystalline (ilmenite and TiO_2 polymorphs in the sample under investigation) and amorphous phases.

During ceramic firing, the crystalline and amorphous phases in the slag undergo thermal oxidation with (re)crystallization of pseudobrookite. This involves Ti^{3+} to Ti^{4+} and Fe^{2+} to Fe^{3+} reactions, leading to the appearance in the optical spectra of typical d–d transitions and a paired enhancement transition of magnetically coupled Fe^{3+} ions in octahedral coordination occurring in adjacent crystallographic sites. Absorbing most of the green to violet light, these bands provoke a colour virage to reddish brown. An additional optical band in the red region, likely due to $Fe^{2+} \rightarrow Fe^{3+}$ IVCT, is responsible of the dark shade.

Titania slag gives rise to an intense brown coloration in low temperature (800–1050 °C) glassy coatings and a suitable light maroon in high temperature (~1200 °C) glazes for porcelain stoneware tiles. The decrease of colour performance is connected with a progressive decomposition of pseudobrookite as the temperature increases. Such a decomposition is accelerated in aggressive media, such as Ca- and Zn-rich glazes used at intermediate temperatures (1100–1150 °C) in the

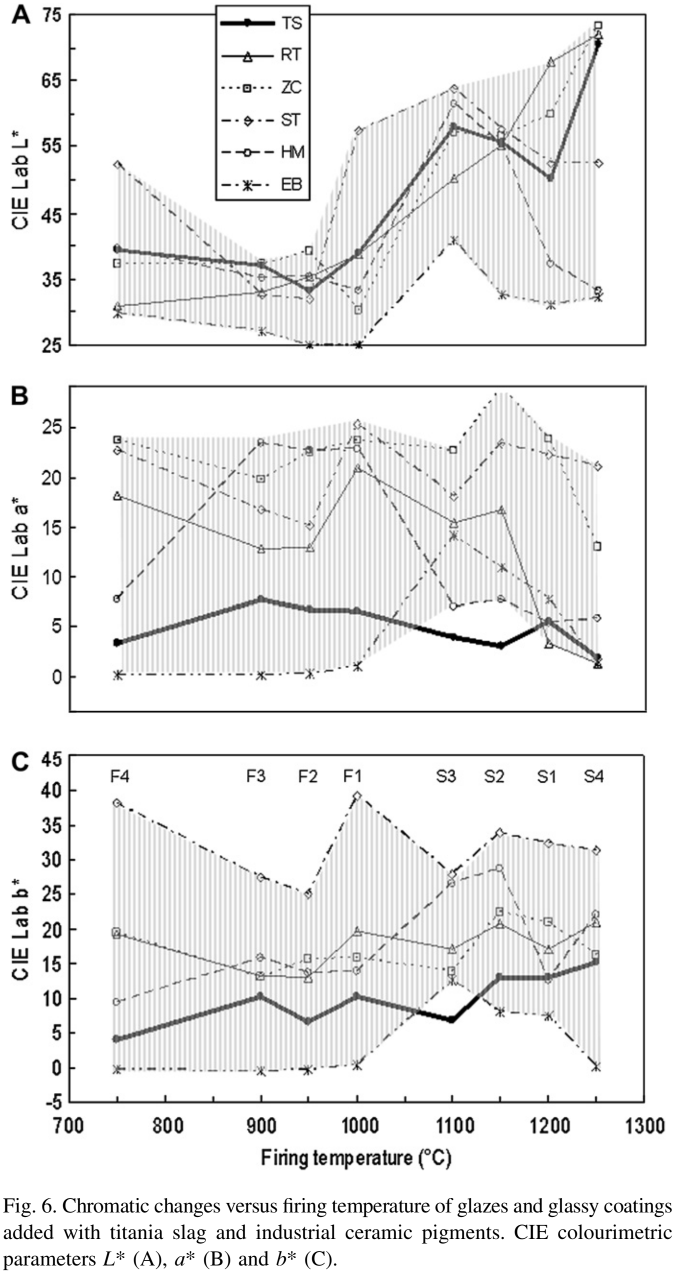

Fig. 6. Chromatic changes versus firing temperature of glazes and glassy coatings added with titania slag and industrial ceramic pigments. CIE colourimetric parameters L^* (A), a^* (B) and b^* (C).

production of wall tiles. The colour performance of titania slag in through-body application is scarce when introduced in pulverized form, but it is appropriate to give desired 'spotting' effects once added in as-received grains.

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