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Effect of firing temperature on the photocatalytic activity of anatase ceramic glazes

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ABSTRACT

The aim of this work was to study the effect of sintering temperature on the photocatalytic activity of anatase ceramic glazes. The glazes were obtained by the addition of titania in two commercial ceramic frits. After mixing, the glazes were sprayed on ceramic tiles, which were fired between 850 and 1000 °C. The glaze surfaces were characterized by scanning electron microscopy and X-ray diffraction. The microstructural analysis showed that the anatase particles can be well dispersed and fixed by the glaze on the tile surfaces. The X-ray diffraction shows that at 850 °C the anatase particles are transformed into rutile. None of the glazes have shown expressive photocatalytic activity due to the transformation of anatase into rutile.

1. Introduction

Photocatalytic semiconductors have attracted much attention, because they are a low-cost and non-toxic alternative to develop photoactive surfaces that could destroy organic compounds by oxidation reactions. In addition, the semiconductor particles can be immobilized in a thin layer on any surface, and can maintain their activity after repeated catalytic cycles [1]. Among various semiconductors available, such as metal oxides (e.g. TiO_2, ZnO, and CeO_2) and metal sulfides (e.g. ZnS or CdS), titania (TiO_2) has been the most suitable for photocatalysis and photovoltaic activity because of its relatively high quantum yield [1,2].

Titanium dioxide has two main catalytically active crystalline phases: anatase and rutile. The anatase form is generally more photoactive and is in widespread practice for environmental applications, such as water purification, recycled water treatment, and air purification [3–9]. Titanium dioxide is also known for properties such as chemical durability, thermal stability, high hardness, applications for white pigments, and resistance to wear, being a material used for the development of protective coatings for ceramic tiles [10–14]. In fact, titanium dioxide is used as a self-cleaning coating on exterior surfaces, as it reduces and decomposes organic pollutants, removing dirt such as grease and oil, thus enabling smaller maintenance costs or efforts [14–19].

Ceramic tiles – tiles for building facades – first undergo a conventional manufacturing process and in sequence, a special layer of glaze can be applied on their surfaces, giving them some properties making them functional coatings. The process of employing an already fired ceramic tile and the application and firing of a new layer (glaze) is currently used in the ceramic industry, a process called “decoration firing,” usually used for aesthetic purposes, such as application of metallic surfaces.

Coatings with catalytic properties, that is, activated by UV radiation, can form surfaces with a number of special features, based on the ability of such coatings to interact with UV radiation. They also change the surface wettability and, therefore, the water deposited naturally or artificially on these surfaces can easily run off [20–22]. Due to their inorganic nature, coatings with catalytic properties are non-combustible and are resistant to conventional cleaning agents. As indicated, their properties are activated by UV radiation, which produces a series of internal changes in the electronic structure of the coating, but does not affect the appearance and the technical characteristics of macroscopic surface (hardness, chemical resistance, etc.). The UV radiation is present in daylight (even without direct sunlight) and partly in some artificial light sources. Therefore, this type of coating is particularly suitable for both exterior and interior areas exposed to enough natural light, or with adequate artificial light sources. The activating effect generated on the surface does not disappear immediately when the radiation ceases, but lasts for a sufficiently long time (longer than the night period) to ensure their effectiveness [23–29].

In addition, some of these coatings significantly increase the contact angle between the workpiece surface and water, thereby favoring the

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formation of drops in which dust particles adhere. The drops easily slide on this surface, bringing together the dirt and helping keep the surface free of inert material (dust, dried vegetable debris, etc.). This effect provides another type of functionality to photocatalytic coatings, to keep surfaces clean and also avoid the proliferation of microorganisms. The hydrophobic coatings used on glass surfaces consist of a combination of organic and inorganic materials with nanometric dimensions, which increase the surface tension, thus contributing to the properties of the surface on which they are applied. On the other hand, some coatings can exhibit the hydrophilic effect, where droplets of water deposited on them decrease their contact angle with the photocatalytic surface after exposure to UV radiation, forming a highly uniform thin film of water, which behaves optically similar to a clear sheet of glass, avoiding the fogging of the surfaces.

The ceramic tile industry is a very large activity worldwide. China produced 7.4 10^9 m^2 and Brazil 0.9 10^9 m^2 of ceramic tiles in 2012, being the major producers [30]. The development of functional surfaces is extremely important for this sector. Thus, it is very important that the conventional manufacturing processes of ceramic tiles are not significantly changed with the development of photocatalytic glazes using regular raw materials and firing conditions.

This work deals with the study of the firing temperature on the photocatalytic activity of anatase glazed tiles. Commercial frits were doped with powdered anatase and were sprayed as ceramic suspensions on ceramic tiles. The coated tiles were fired and their photoactive properties were determined over time.

2. Experimental

2.1. Frit and anatase characterization

In this work, two commercial frits (TEC, a borosilicate glaze, and SMT, a calcium based glaze), halite (NaCl) and commercial anatase were used. The frits were chemically (by XRF and AAS for B element) and thermally (by optical dilatometry, 40 °C/min, air atmosphere) characterized. For anatase, the chemical composition (XRF), particle size (laser diffraction), and crystalline structure (XRD, Cu K_α ($\lambda = 1.5418$ Å), 40 kV and 30 mA, 2θ from 10 to 90°, 0.05° step, and 1 s time) were determined.

2.2. Glaze preparation

The photoactive glazes were prepared with a 3:7:10:80 ratio of TiO_2, frit or halite, dispersant, and water (wt.%), respectively, and the formulations were vigorously stirred for subsequent deposition on ceramic tiles. The suspensions were applied by spraying on stoneware tiles (10 cm × 10 cm) already glazed and the tiles were fired between 850 °C and 1000 °C for 1 h cycle in a laboratory muffle furnace for 20 min at the maximum temperature.

2.3. Glaze characterization

After firing, the tiles were characterized by scanning electron microscopy (SEM). The hydrophilic (or hydrophobic) effect of the anatase glazes was determined by measuring the water contact angle formed on the tile surface at different UV-irradiation times using acontact angle goniometer system.

The phase analysis was determined by powder diffraction using a control unit with a vertical goniometer. The instrument was equipped with a graphite diffracted beam monochromator and a copper radiation source (λ ($K_{\alpha1}$) = 1.5406 Å), operating at 40 kV and 30 mA. The X-ray powder diffraction pattern (XRPD) was collected by measuring the scintillation response to Cu K_α radiation versus the 2Θ value over a 2Θ range of 5–55, with a step size of 0.02° and a counting time of 4 s per step.

2.4. Photocatalytic analysis

The photocatalytic activity of the samples was determined by easuring the variation of methylene blue (MB) concentration in queous solution (5 vol.%) in contact with the coated samples under UV rradiation in comparison with an uncoated sample. Initially, the samples were kept for 30 min in the dark to enable the MB solutions to be adsorbed onto the samples' surface. The absorbance of the methylene blue solutions (6 mL) was determined in a UV–visible spectrometer at 664 nm wavelength using water as the reference with the sample solutions collected during time intervals (up to 5 h). MB was chosen to simulate the degradation of organic matter by the anatase glaze and, therefore, to estimate the glaze efficiency as a self-cleaning product.

3. Results and discussion

3.1. Frit and anatase analysis

The chemical analysis (XRF and AAS) of the frits is shown in Table 1. TEC frit is a borosilicate glass with sodium and zinc oxides; the loss on ignition is probably due to the presence of water. The SMT frit is composed by silica and calcium oxide with a small addition of borate and sodium and potassium oxides; the high alumina content results in a higher softening point for this frit. Halite is a salt (NaCl, 99.5% purity).

The thermal behavior of TEC and SMT frits and halite determined by optical dilatometry is shown in Table 2. TEC frit is more suitable for a third-firing process than SMT due to its lower softening and melting temperatures thanks to its chemical composition. The SMT frit is more refractory than TEC one because of its higher alumina and silica and lower borate contents, besides its high calcium oxide content. In turn, halite shows an intermediate behavior in comparison with TEC and SMT frits, with a small gap between the sintering and melting points, thus making it not suitable for industrial use due to the great viscosity variation in a narrow temperature range. In addition, the release of Cl species during firing promotes the formation of HCl and subsequent corrosion of all machinery. Although widely used in the fabrication of industrial frits in Brazil, the use of halite is not appropriate in the ceramic industry but they are studied due to their use in some types of glazes.

Regarding the TiO_2 powder, the XRD analysis has confirmed that it is mostly composed by anatase (90% by Rietveld analysis). The particle-size distribution analysis indicates that the anatase powder is submicrometric. Some TiO_2 catalysts, such as the Degussa P25, are a mixture of nano and submicron powders with anatase and rutile as main phases.

3.2. Glaze analysis

Fig. 1 presents SEM images of the ceramic tile surfaces after spraying of the anatase glazes and third firing. At 850 °C (Fig. 1a), the glaze composed by halite and anatase does not form a homogeneous layer that could cover the entire tile surface. The glaze apparently did not soften or stretch on the surface, remaining as a pre-glaze on the surface of the sintered samples. At 900 °C (Fig. 1b), the glaze is more homogeneous, but still presents some particles on the surface.

The SMT/anatase glaze fired at 850 °C (Fig. 1c) also depicts a granular aspect, typical of a non-softened glaze. At 900 °C (Fig. 1d), the glaze presents the same aspect as it does at 850 °C. The microstructure of the

Table 1
Chemical analysis of the frits (by XRF and AAS).

Oxide (%)	SiO_2	B_2O_3	Na_2O	ZnO	Al_2O_3	TiO_2	K_2O	CaO	MgO	LoI
TEC	52.7	22.6	11.0	4.8	3.8	2.3	0.5	0.2	0.1	1.3
SMT	63.2	6.8	2.5	0.1	10.2	–	4.7	10.3	1.3	0.5