Open Ceramics 6 (2021) 100091

Contents lists available at ScienceDirect

Open Ceramics

journal homepage: www.editorialmanager.com/oceram

Preparation and characterization of glass ceramic frits with high solar reflectance

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ARTICLE INFO

Keywords:
Solar reflectance
Glass ceramics
Ceramic tiles
Engobes

ABSTRACT

The temperature of cities increases due to the UHI phenomenon and climate change. Among the mitigation strategies, high solar reflectance materials make an important contribution, in particular ceramic materials on which studies have shown that the functionalization of the ceramic engobe allows to increase solar reflectance (SR). This study attempted to improve the SR of ceramic tiles, starting from studies correlating the heat treatment temperatures of glass-ceramic frits with SR, because frit is fundamental for the preparation of an engobe, which plays, as some studies have shown, an increasingly important role in solar reflectance. Five glass-ceramic frits have been analysed: four of these are commercial frits, while one has been obtained and optimized experimentally.

1. Introduction

Cities have become "Urban Heat Islands (UHI)", a microclimatic phenomenon that affects metropolitan areas, where temperatures are considerably higher than in the surrounding rural areas [1–3]. Over the years, mitigation strategies have been developed to fight this phenomenon. Many new techniques have been proposed, but especially high albedo materials have had a strong echo: known as "solar reflective materials", they are used to cover the building envelopes and urban floors and they have been studied to better reflect solar radiation, showing a great potential to fight against the effects of Urban Heat Island: these are highly reflective roofing materials that absorb less heat and stay cooler than traditional coatings if exposed to solar radiation [3].

In particular, ceramic materials are considered solar reflective materials and represent an interesting solution for several reasons: excellent durability over time, naturally high thermal emissivity ($\varepsilon = 0.90$), high resistance to soiling thanks to the ceramic glaze coating that facilitates cleaning and reduces maintenance costs [4]. Another very important aspect is that, unlike other organic products, ceramic tiles have a higher reflectivity spectrum in the NIR region [5].

An advanced cool color product (solar reflective materials characterized by a colored response in the visible wavelength range) requires the use of a support, a high solar reflectance basecoat and a transparent solar radiation topcoat [4,6]. The study conducted by Ferrari et al. (2013) describes the development of a completely innovative product, i.e. glazed ceramic tiles with high solar reflectance obtained through a process of functionalization of the engobe, which represents the NIR-reflective basecoat [7]: in this work the solar reflectance values have been increased thanks to the introduction of white ceramic pigments, respectively Zirconium Silicate ($ZrSiO_4$) and Titanium Dioxide (TiO_2) which, due to their high refractive index, significantly affect the solar reflectance [7].

It should be pointed out that a ceramic engobe is a clayey mixture, composed of natural raw materials, glass frits and additives and, in this study, in order to make it functional, it was decided to optimise the frit; in particular, industrial glass ceramic frits were used, modifying their formulation, with the aim of obtaining a final glass ceramic with high solar reflectance values. This choice was made because glass ceramics are polycrystalline materials, prepared from glass products and obtained through a controlled process of nucleation and growth, which produces crystallisation [8]: therefore, the purpose of this study was to verify the effect of the crystalline phases that form in the frit during heat treatment on the final solar reflectance values of the ceramic product.

2. Materials and methods

Four industrial glass ceramic frits supplied by the company COLOROBBIA ITALIA S.P.A. have been selected, each with a different composition, called CMAS (CaO, MgO, Al_2O_3, SiO_2), CZS (CaO, ZrO_2, SiO_2), CBS (CaO, BaO, SiO_2) and CZAS (CaO, ZrO_2, Al_2O_3, SiO_2) respectively; then a

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https://doi.org/10.1016/j.oceram.2021.100091
Received 30 September 2020; Received in revised form 15 February 2021; Accepted 14 March 2021

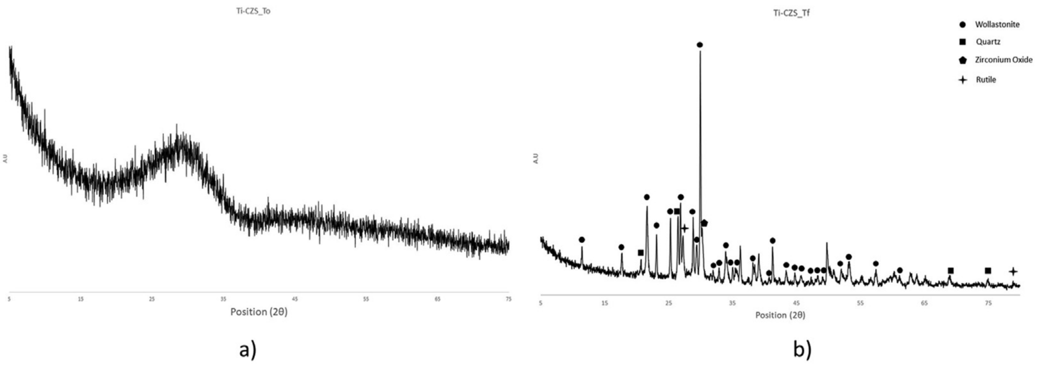
Table 1
Comparison of the most significant SR values of the CZS (T_o, T_c, T_f = 940 °C, 1010 °C, 1100 °C) and Ti-CZS (T_o, T_c, T_f = 929 °C, 1006 °C, 1065 °C) samples obtained with a UV-VIS-NIR spectrophotometer.

	Sol (CZS)	Sol (Ti-CZS)	NIR (CZS)	NIR (Ti-CZS)
T_o	0.875	0.948	0.933	0.979
T_c	0.667	0.919	0.703	0.962
T_f	0.702	0.889	0.732	0.961

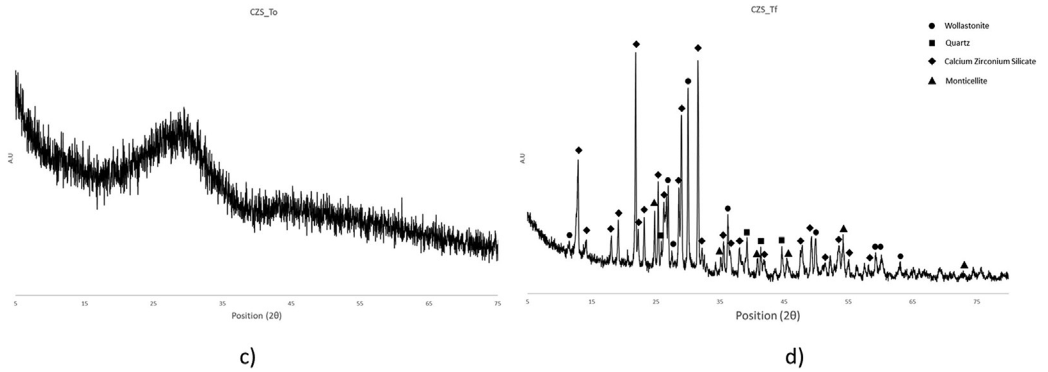
new frit has been made, obtained by modifying CZS, adding titanium oxide (TiO_2): this experimental frit will be called Ti-CZS and its oxides composition, expressed in wt%, is the following: $\mathbf{SiO_2}$ = 53.9, $\mathbf{Al_2O_3}$ = 0.3, **CaO** = 31.8, **MgO** = 0.5, $\mathbf{ZrO_2}$ = 8.2, $\mathbf{TiO_2}$ = 5.30. To obtain Ti-CZS, CZS was modified by replacing half the weight of ZrO_2 with TiO_2; then, the raw materials were weighed, mixed for 30 min, transferred into a melting pot of mullite and melted at 1450 °C in a resistance melting furnace by the following heat treatment: 10 °C/min up to 900 °C, 1 h isotherm at 900 °C, then 10 °C/min up to 1450 °C with 1 h isotherm.

Then the frit was quenched in water, ground and pressed to obtain cylindrical samples with a diameter of 40 mm, 5 mm thick and 10 g in weight; then the samples were dried in a stove. Wet grinding was carried out, using two porcelain jars and alumina balls: each jar was filled with 150 g of frit and 100 g of water; then, through a grinder mill, the content was ground in 60 min. After drying the powder in the stove, it was collected and pressed. The pressing was carried out using a laboratory hydraulic press, set at a pressure value of 35 MPa, in order to make the pressing conditions as uniform as possible for each sample, because the pressure is a variable that affects the sintering process during heat treatment of the pressed products [8].

To carry out the heat treatments, it was first necessary to determine the characteristic temperatures of the different glasses used: T_{onset} (T_o) is the temperature measured just before crystallisation; $T_{crystallisation}$ (T_c) is the peak temperature; T_{final} (T_f) is the temperature measured after the peak value has been exceeded. This analysis was carried out through DSC



Symbol	Ref. Code	Score	Compound name	Chemical formula
●	01-084-0655	60	Wollastonite-2\ITM\RG	$CaSiO_3$
■	01-074-1811	35	Quartz	SiO_2
⬟	01-079-1769	37	Zirconium Oxide	ZrO_2
✦	01-077-0445	21	Rutile, syn	TiO_2



Symbol	Ref. Code	Score	Compound name	Chemical formula
●	01-084-0655	45	Wollastonite-2\ITM\RG	$CaSiO_3$
◆	00-039-0194	62	Calcium Zirconium Silicate	$Ca_2ZrSi_4O_{12}$
▲	01-084-1326	26	Monticellite	$CaMgSiO_4$
■	01-081-1665	18	Quartz	SiO_2

Fig. 1. XRD patterns for samples Ti-CZS at T_o (a), Ti-CZS at T_f (b), CZS at T_o (c) and CZS at Tf (d).

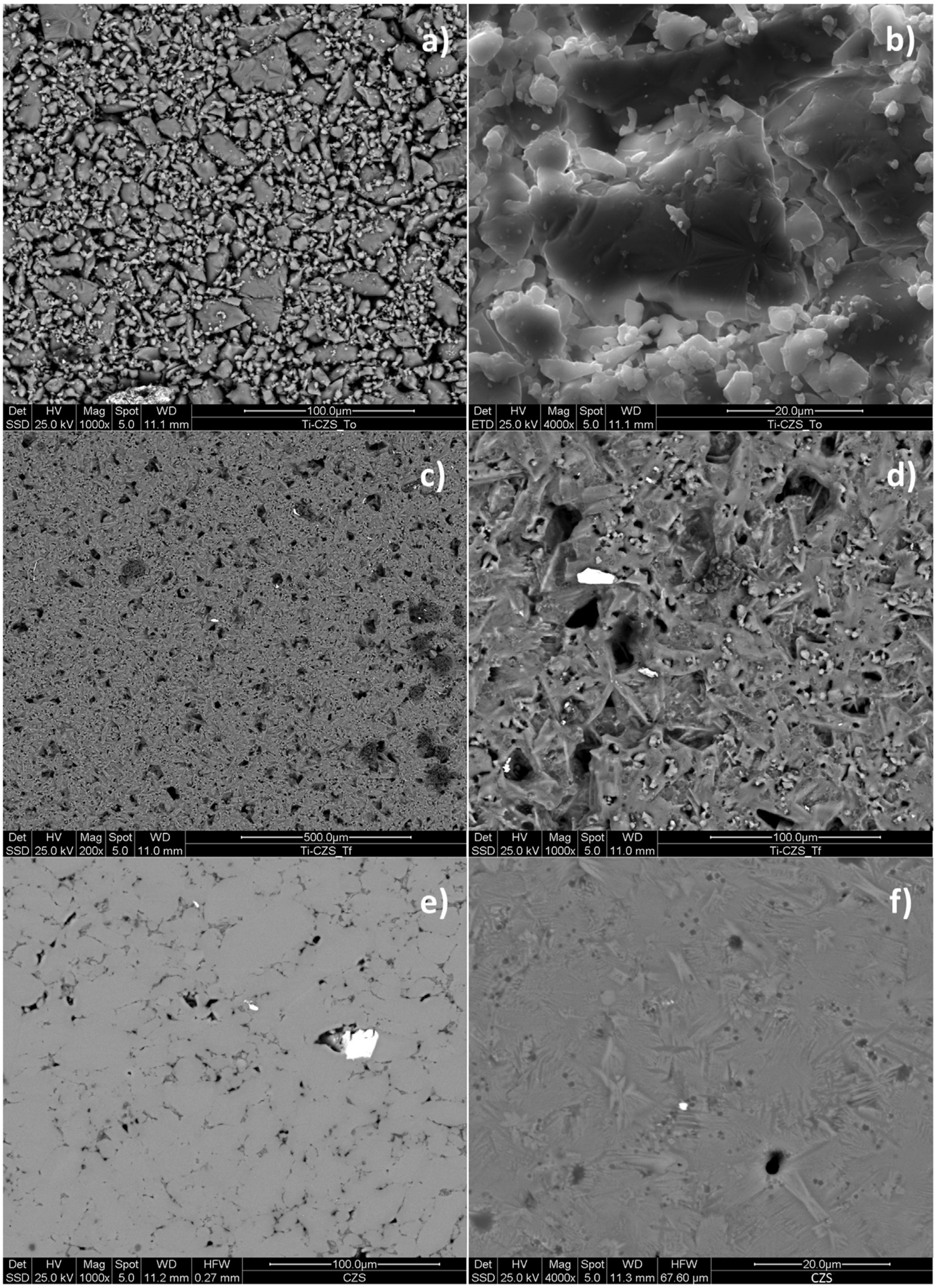


Fig. 2. SEM micrographs at different magnifications of Ti-CZS samples at T_o temperature (a, b) and T_f temperature (c, d): (a) sample surface mag. 1000x, (b) detail of crystallisation mag. 4000x, (c) sample surface mag. 200x, (d) sample surface mag. 100x; SEM micrographs of CZS samples at T_o (e) and T_f (f) temperature: (e) sample section mag. 1000x, (f) sample section mag. 4000x.

(Differential Scanning Calorimetry). Then, the cylindrical samples were subsequently heat-treated in a laboratory electric furnace increasing the temperature by 10 °C/min until the set temperature was reached, then 1 h of isotherm and, finally, slow cooling to a temperature below 200 °C. In this way, glass-ceramic buttons have been obtained, on which all the necessary characterizations have been made: Solar Reflectance (SR), X-Ray Diffractometry (XRD), Scanning Electron Microscopy (SEM).

3. Results and discussion

The solar reflectance measurements have been made on all the glass-ceramic samples but, in this section, only the most relevant ones are reported, related to the CZS commercial frit and the Ti-CZS experimental frit, as the recorded SR values were the most promising. The DSC analysis on Ti-CZS powders provided the characteristic temperatures for the heat treatments on the presses (respectively $T_o = 929$ °C, $T_c = 1006$ °C, $T_f =$

1065 °C) and, at these temperatures, glass-ceramic samples were obtained; instead, the DSC analysis on CZS powders provided the characteristic temperatures at which three glass-ceramic samples were obtained (respectively $T_o = 940$ °C, $T_c = 1010$ °C, $T_f = 1100$ °C). The solar reflectance tests were carried out on the samples and, as shown in Table 1, the results were quite promising, although with a decreasing trend from T_o to T_f. The interesting aspect of these analyses was how the Ti-CZS samples showed an increase in SR values compared to the CZS samples, as shown by the comparison in Table 1.

The SR values of the samples were measured with a UV–Vis-NiR spectrophotometer in the 250–2500 nm range, according to the ASTM E903-12 standard, and the AM1GH spectrum was used to calculate the solar reflectance values. The measurement error is about 0.01. The solar reflectance (ρ_{sol}) is calculated by integrating the spectral reflectance (ρ_λ, measured value) between 300 and 2500 nm, weighted by the standard spectral irradiance of the sun relative to the earth's surface ($I_{sol,\lambda}$):

$$\rho_{sol} = \frac{\int_{300}^{2500} \rho_\lambda \cdot I_{sol,\lambda} d\lambda}{\int_{300}^{2500} I_{sol,\lambda} \, d\lambda}$$

These high values, recorded mainly in the VIS-NIR region (400–2500 nm), are due to the presence of TiO_2 and ZrO_2, both ceramic pigments with high refractive index. Therefore, Ti-CZS frit, with respect to solar reflectance, has been considered suitable for further investigation, as well as for its subsequent use in ceramic engobes with improved solar reflective performance. The XRD analysis was particularly relevant for ceramic glass treated at T_o and T_f temperatures, as the T_f temperature was considered a summary temperature of what happens during the T_c treatment: in fact no great differences were observed between the crystalline phases detected in the samples treated in this way. The diffraction patterns of the Ti-CZS and CZS samples (Fig. 1) show their mineralogical evolution: at temperature T_o the sample still maintains a strongly glassy structure, while at temperature T_f the crystalline phases are formed (Wollastonite, Quartz, Zircon Oxide, Rutile (b), Wollastonite, Calcium Zirconium Silicate, Monticellite, Quartz (d)).

Knowing that SR is highly dependent on heat treatment and comparing the XRD results with the solar reflectance measurements made on the Ti-CZS samples, it can be observed that the crystallisation process does not favour an increase in SR values: in fact, the most solar reflective sample remains the Ti-CZS at T_o temperature, which is also the most glassy. Therefore, the refractive index of the glass remains higher than the refractive index of the crystalline phases. In particular, it has been observed that the reflectance of Ti-CZS at T_o temperature increases compared to the basic CZS frit due to the addition of TiO_2. Finally, it should be noted that the high solar reflectance certainly depends on the refractive index of the crystalline phases, but also on the difference in refractive index between the glass phase and the crystals, the size of the crystals and their concentration (in fact, the glass/crystal ratio and the size of the crystals can greatly influence the SR). The SEM images on the Ti-CZS samples reveal that, at T_o temperature, the powders fail to sinter, remaining predominantly glassy (and this confirms what was observed in the mineralogical analysis); however, as shown in Fig. 2 (b), there is a beginning of crystallisation. On the other hand, at T_f temperature, the images reveal that the powders are more sintered than in the previous case and some crystalline phases have formed, in particular, we can observe crystalline formations of Wollastonite and Zirconium Oxide, as also confirmed by the mineralogical analysis. CZS sample at T_o temperature (Fig. 2 (e)) confirm what is shown in the XRD analysis: the material is mainly glassy, but there are some very clear crystalline phases rich in Zirconium and Oxygen, most likely ZrO_2: it is therefore possible that the high quantity of ZrO_2 in the glassy phase and the presence of small crystals of ZrO_2 produced the high solar reflectance of the sample. The section of the CZS sample at T_f temperature (Fig. 2 (f)) confirms once again the XRD analysis: in fact, the formation of a crystalline structure between the glassy matrix can be observed, as is typical of a glass-ceramic material: in particular, it is possible to distinguish Wollastonite crystals from the typical elongated shape.

The proposed frit was developed and studied to be included in the formulation of a ceramic engobe for porcelain stoneware tiles, usually fired at temperatures around 1200 °C: because of this, the behaviour of Ti-CZS glass ceramic sample at T_o temperature (not been well sintered) is not a problem since the frit will certainly sinter and crystallize at firing temperatures. In any case, even at the highest temperature ($T_f = 1065$ °C), Ti-CZS has shown high SR values confirming itself as the best and therefore suitable for producing reflective solar engobes.

4. Conclusions

In conclusion, with this work it was observed that the modification of the CZS frit with the addition of a percentage of TiO_2 produced Ti-CZS glass ceramic samples with reflectance values much higher than those shown by the CZS samples: this was a positive result, as it allowed to identify the Ti-CZS frit as a possible candidate for the subsequent production of an engobe with potential improved solar reflective performance. It is important to highlight, however, that this study was carried out to see the evolution of SR during a frit sintering process and to evaluate if SR can be influenced by different factors (presence of glass/crystalline phase, morphology of particles, chemical composition): this represents a preliminary study on the solar reflective role of frits in view of their use in ceramic engobes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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