POST 103THIN LZSA GLASS-CERAMIC GLAZE LAYERS FOR DOUBLE FAST FIRING CERAMIC FLOOR TILES

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1. Introduction

Glass-ceramics are polycrystalline solid materials containing residual glassy phase.[1,2] Such materials show several interesting properties, and have found applications in different areas of society and industry, such as cooktops, cookware and bakeware, protection layers, and sewing-thread supports in the textile industry.[1-3] These materials have also found application in the ceramic tile field. In fact, successful examples of such application are the trademarks “Neoparies” and “Enduro”.[1,4] Among glass-ceramic systems of practical interest the LZS (Li_2O-ZrO_2-SiO_2) stands out since the obtained glass and the formed crystalline phases, zircon ($ZrSiO_4$) and lithium dissilicate ($Li_2Si_2O_5$), provide glass-ceramic materials with adequate properties for applications such as glazes for ceramic tiles. Previous research works carried out by the authors[5-10] showed that certain compositions of the LZS system exhibit, in particular, high bending strength as well as high abrasion and chemical resistances when compared to traditional materials. Moreover, they are initially white materials, and allow to be colored by the introduction of an appropriated inorganic pigment. They are produced at lower temperatures (800-900^{o}C) in short times (35-60 min) using the same conditions and machines of a traditional ceramic factory. However, the utilization of this system is limited by the high coefficient of thermal expansion, CTE (9-11$\times10^{-6}$ $^{o}C^{-1}$), in comparison to the ceramic supports (5.5-7.0$\times10^{-6}$ $^{o}C^{-1}$). Therefore, considering that the global CTE of the ceramic system depends on the intrinsic properties of each present crystalline phase, the partial substitution of zirconia by alumina was tested to form the β-spodumene$_{ss}$ (β-spodumene solid solution, $Li_2O\cdot Al_2O_3\cdot 4\text{-}10SiO_2$) crystalline phase.[11-13] The β-spodumene ($Li_2O\cdot Al_2O_3\cdot 4SiO_2$) crystalline phase shows low CTE (0.9$\times10^{-6}$ $^{o}C^{-1}$). An appropriate crystallized amount of β-spodumene could compensate the effects caused by other formed crystalline phases, such as zircon (4$\times10^{-6}$ $^{o}C^{-1}$) and lithium dissilicate (11$\times10^{-6}$ $^{o}C^{-1}$), in particular, decreasing the CTE of the material and originating thus a new glass-ceramic system named LZSA (Li_2O-ZrO_2-SiO_2-Al_2O_3) based mainly on β-spodumene and zircon crystalline phases.[11-13] In this context and considering the peculiar properties of LZSA glass-ceramics according to our previous papers, this work show results regarding thin LZSA glass-ceramic layer glazes obtained by the double fast firing technology. A concentrated suspension containing LZSA parent glass powder and a polymeric liquid base was prepared and applied on fired ceramic bodies by using the serigraphy technique. The double firing was conducted in a roller kiln at the 700-1000°C temperature range and firing times between 30 and 120 min. Powder samples were chemically analyzed by X-ray fluorescence (XRF). Sintering behavior of glass compacts was evaluated by thermal shrinkage measurements in an optical dilatometer (DIL). Crystallization temperature was determined by differential thermal analysis (DTA) and microstructure and glaze layer thickness by scanning electron microscope (SEM). Finally, finished ceramic floor tile samples were evaluated by applying typical ceramic tests. Results indicated that the double fast firing technology, in this case, is an appropriated technical solution to obtain sintered thin glass-ceramic glaze layers to produce high performance ceramic floor tiles for a given application.

Key words: *glaze, glass-ceramic, ceramic, ceramic floor tile.*

2. Experimental procedures

A LZSA glass-ceramic frit ($19Li_2O\mathbf{.}8ZrO_2\mathbf{.}64SiO_2\mathbf{.}9Al_2O_3$-molar basis) obtained by melting (1500°C/7h) of industrial raw materials ($ZrSiO_4$, Li_2CO_3, quartz and natural spodumene) was wet milled in laboratory alumina ball mill (45 h) so that a powder with a average particle size of 10 µm was found by laser scattering analysis (CILAS 1064 L). Chemical composition of the LZSA glass powder was determined by X-ray fluorescence spectroscopy (Philips, PW 2400) and by atomic absorption (UNICAM, Solar 969) for the lithium determination. Thermal linear shrinkage (TLS) of compacted samples was measured by using an optical dilatometer (Expert System Solutions, MISURA ODHT) at 10°C.min^{-1} in air.

The crystallization temperature of the glass powders were measured using differential thermal analysis, DTA (Netzsch, STA EP 409) in air at a heating rate of 10°C.min^{-1} using powdered specimens of about 60 mg in an alumina sample holder with an empty alumina crucible as reference material.

Subsequently, a concentrated suspension containing 56 wt.% LZSA glass powder and 44 wt.% organic media (TF 057/A Manchester) was prepared for serigraphic applications on fired industrial ceramic floor tiles. After serigraphic applications (110 g/m^2) ceramic samples were dried at 110ºC for 2 h and then they were fired in a roll kiln in the 700-1000ºC temperature range for 5 min at the maximum temperature so that the total cycle was took from 30 to 120 min, respectively. Selected fired samples were coated with a thin Au film for scanning electron microscopy (SEM) observations (Model Philips XL-30). Additional selected samples were prepared and subjected to typical tests applied to ceramic tiles i.e., chemical resistance, staining resistance, abrasion wear resistance and friction coefficient (Tortus method) according to ISO 10545. The roughness on glazed surfaces before and after abrasion wear was also evaluated.

3. Results and Discussion

Figure 1 shows the linear shrinkage curve of a LZSA glass compact. From Figure 1 it can be seen that densification, represented by the liner shrinkage, starts at about 600ºC in close agreement to the glass transition temperature (~600ºC) determined by DTA, attaining maximum at 850°C when the shrinkage rate tends to zero. This behavior is related, initially, by the crystallization mainly of zircon, lithium silicates and β-spodumene crystalline phases according to XRD analysis in our previous research works[11-13]. At higher temperatures (>1000°C) crystalline phases are completely melted as shown in Figure 1, since shrinkage increases. This behavior was confirmed also by DTA.

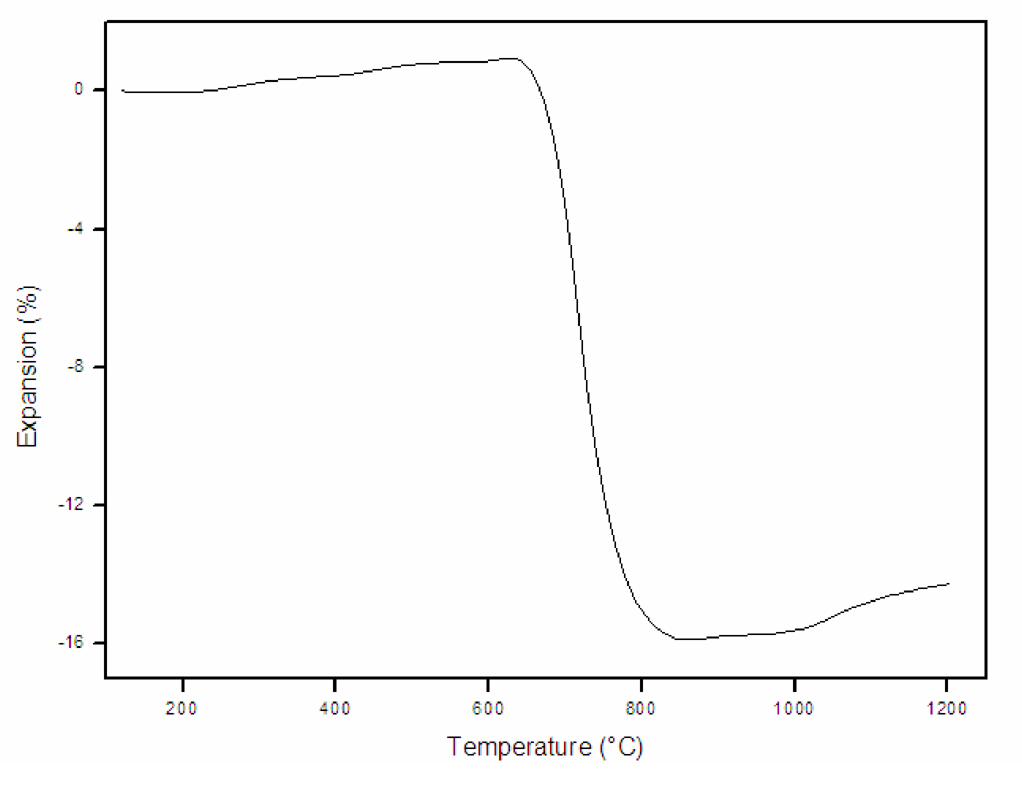
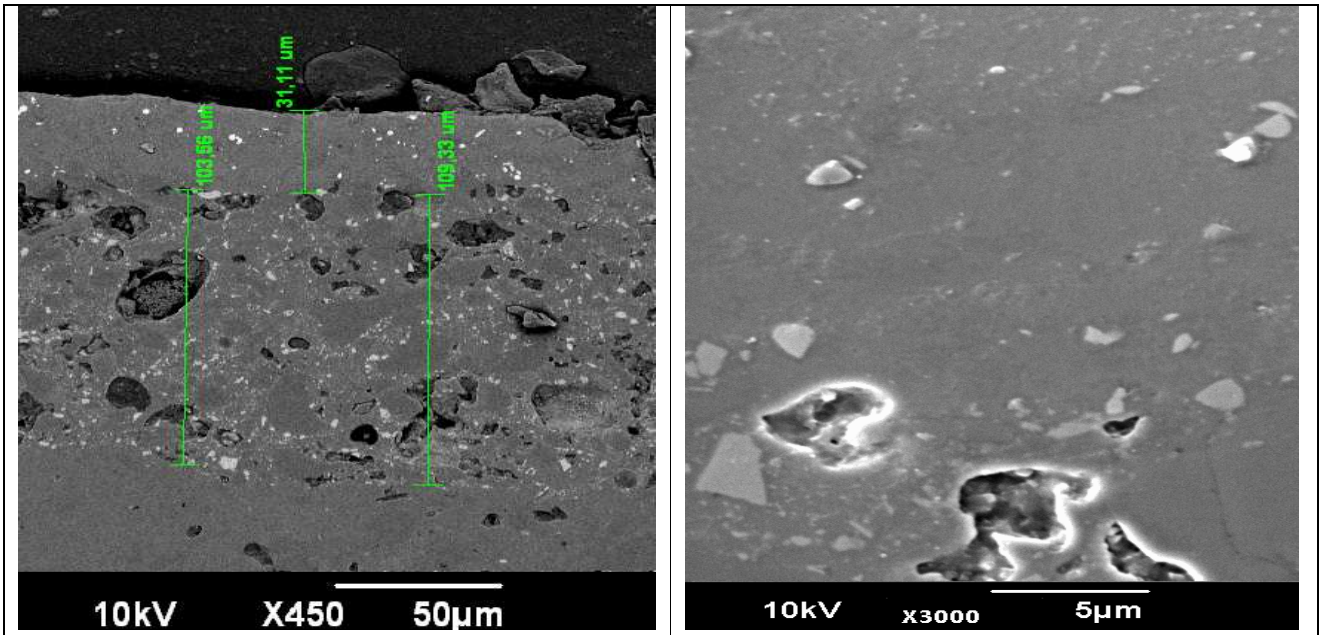


Figure 1. Linear shrinkage of a LZSA glass compact. Heating rate 10ºC.min^{-1}.

According to Figure 1, DTA and microstructural analysis selected samples were fired at 800ºC for 5 min since this was the best condition in terms of porosity and dimensional stability.

In fact, Figure 2 shows SEM micrographs related to a sample fired at 800ºC for 5 min in which is possible to see a very dense and thin (average thickness of 30 µm) LZSA glaze layer respect to the engobe layer and the ceramic body. It is important to point out that the thickness of industrial glazes for ceramic tiles corresponds to about 75-500 µm so that 500 to 750 g/m^2 of suspensions are applied.

Preliminary staining tests using chromium and iron oxides on abraded surfaces, after 12,000 revolutions in the abrasion test equipment, show non staining points indicating that is possible to obtain glazed ceramic floor tiles with optimized porosity for a specific application. Chemical resistance tests show best results (class AA). The measured coefficient of friction was approximately 0.64 in the dry and 0.59 in the wet conditions, respectively.



(a) (b)

Figure 2. SEM micrographs of the cross sections of samples fired at 800ºC for 5 min at (a) low magnification (ceramic body, engobe-intermediate layer , LZSA glaze-top) and (b) at higher magnification evidencing the LZSA glaze layer on the engobe.

Abrasion wear e chemical resistances results are directly related to the crystalline phases mainly zircon since it has relatively high hardness (7.5 in the Mohs scale) and chemical stability. The high staining resistance, on the other hand, is related to the low porosity observed on the LZSA glazed surfaces and also to the relatively low measured roughness. In fact, surfaces before and after abrasion wear show roughness (Ra) values of 1.44 µm and 1.74 µm, respectively.

4. Conclusions

LZSA glass-ceramic glazed ceramic floor tiles were obtained by double fast firing at 800ºC for 5 min. Relatively thin (30 µm) and low porosity glazed layers, applied by the serigraphy technique, containing mainly zircon and aluminosilicates crystals were obtained after firing process.

The obtained ceramic floor tiles did not show staining points even after 12,000 revolutions in the abrasion test equipment.

Chemical resistance was class AA being that the coefficient of friction can be appropriated for antislip applications.

On the bases of the preliminary obtained results it is possible to say that the produced ceramic floor tiles are potential candidates in a number of applications but in particular in cases where cleaning is an important requirement.

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