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Effect of some additives on the development of spinel-based glass-ceramic glazes for floor-tiles

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Abstract

The feasibility of developing spinel-based glass-ceramic glazes from a glass with composition in the system $ZnO–MgO–B_2O_3–Al_2O_3–SiO_2$ was examined. To do it additional fluxes and/or nucleants were added to a parent glass before melting. Pressed pellets of powdered glasses were submitted to standard thermal treatments up to 1200 °C. The crystallization path and the microstructural development at several temperatures were followed by several experimental techniques. The results showed that additions of TiO_2 as nucleant or additional B_2O_3 as flux to the chosen glass favored the crystallization of cordierite or mullite as main crystalline phase. Glasses which also contained minor amounts of Na_2O and K_2O, as additional fluxes, crystallized rapidly to spinel $(Mg,Zn)Al_2O_4$ using a single relatively fast heating ramp without a previous nucleating heat treatment step. Microstructural examination revealed that a uniform, fine-scale phase separation preceded crystallization. Very small, well-shaped crystals of spinel with octahedral morphology were formed. Slips of these glasses on conventional tile supports thermally treated under single heating ramps developed similar microstructures that the ones raised from pellets. This feature allows to suggesting these spinel-based glass-ceramic glazes as good candidates to improve the mechanical properties of conventional glazes.

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1. Introduction

Glass-ceramics are composed materials of one or more crystalline phases immersed in a residual glassy phase. Their in general outstanding properties have given rise to a wide variety of applications [1]. Glass-ceramic processing has been carried about starting both from bulk glasses and from powder [2].

As it is well known ceramic tiles are materials consisting of two layers, the inner one based on a sintered mixture of powders and the surface layer, i.e. outer one that we see, that in general consists of a mixture of several vitrified oxides and inorganic additives, termed glaze. The final properties of these materials are very dependent on the glaze properties. Nowadays, there is an increasing demand of new ceramic tiles which have improved technical properties compared with those of their parent glasses, encompassing high resistance to wear by abrasion, high surface hardness, low level of closed porosity and good chemical resistance. This means, therefore, to improve the properties of glazes. A possible and interesting way to manufacture wall- and floor-tile materials with better mechanical, chemical and optical can be accomplished by replacing the glaze layer by a glass-ceramic one.

A number of papers have been published during last years dealing with the feasibility of preparing glass-ceramic glazes based on cordierite, pyroxene and β-spodumene solid solution [3–6]. More recently

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mullite-based glass-ceramics have been reported [7,8]. Considering the intrinsic physical properties of the spinel crystalline phase, it would be interesting to develop spinel-based glass-ceramic glazes [9].

Glass-ceramics based on spinel compositions ranging from gahnite ($ZnAl_2O_4$) toward spinel ($MgAl_2O_4$) were obtained by controlled crystallization of glasses in the $ZnO–MgO–Al_2O_3–SiO_2$ quaternary system, and adding ZrO_2 and/or TiO_2 as nucleating agents [10]. However, even though the crystallization of spinel is possible for the above reported compositions, the glass-ceramic glaze application would require controlling simultaneously the spinel crystallization and the glaze maturing in the temperature range between 1100 and 1200 °C. In order to reach full development of the glass-ceramic glaze layer, it is necessary to add certain fluxes which allow the glass to mature properly, i.e. the glaze should have a suitable surface tension to minimize crawling of the coating away from the edges or any hole that are present on firing. Likewise, to control the amount of crystallization and the size and shape of crystals nucleating and/or fluxes agents should be also added.

The approach followed to check the feasibility of these spinel-based glass-ceramic glazes is to choose a reference composition in the $ZnO–MgO–B_2O_3–Al_2O_3–SiO_2$ system and to introduce fluxes and nucleating which allowing to develop this type of composed glazes at temperatures up to 1200 °C by single heating ramps without a previous nucleating heat treatment step.

In this paper we report results on the effect that some additives (such as B_2O_3, Na_2O, K_2O and TiO_2) added to a chosen parent glass, have on the crystallization path to the final spinel crystalline phase and also the microstructural features of that final spinel-based glass-ceramic glaze.

2. Experimental procedure

2.1. Preparation of glasses

Based on previous experiments, for this study it was chosen a reference glass of composition, in wt%, $53SiO_2$, $29Al_2O_3$, $9MgO$, $6B_2O_3$ and $3ZnO$. The reference glass is referred as sample A. Glasses from B to E contain additional nucleant and/or fluxes. The nucleant used is TiO_2 and the fluxes are additional B_2O_3 and/or a mixture of Na_2O and K_2O in a wt ratio of 1–3. The used nomenclature for all glasses is shown in Table 1. Glasses of the five compositions were obtained by melting mixtures of the required amounts of SiO_2, Al_2O_3, $MgCO_3$, ZnO, TiO_2, BO_3H_3, Na_2CO_3 and K_2CO_3, all high quality reagents provided from Merck, at 1600 °C for 2 h. Melted glasses were poured into cold water and, after regrinding they were remelted again. After the second melting a portion of the melt was poured into water and milled up to obtain a powder glass with particle size smaller than 30 μm.

Table 1
Composition and nomenclature of prepared glasses (wt%)

Oxide	Glass				
	A	B	C	D	E
SiO_2	53.0	51.0	49.1	53.0	51.0
Al_2O_3	29.0	27.9	26.9	26.0	25.0
MgO	9.0	8.7	8.3	9.0	8.7
ZnO	3.0	2.9	2.8	3.0	2.9
TiO_2	–	3.8	3.7	–	–
B_2O_3	6.0	5.8	5.6	9.0	8.7
K_2O	–	–	2.8	–	2.9
Na_2O	–	–	0.9	–	1.0

The feasibility for developing spinel-based glass-ceramic glazes with the above glasses was investigated by heating cylindrical pellets of loosely pressed powder, i.e. under a pressure of about 5 MPa. These glass powder pellets were thermal treated by a single heating step at several temperatures up to 1200 °C for 2 h. The heating rate used was 10 °C min^{-1}. These conditions were chosen to simulate those in an industrial application of the glaze layer, as for the fabrication of ceramic tiles. Moreover, in order to check the correct maturing of compositions as glazes they were prepared as slips and used to glaze some conventional tile support.

2.2. Techniques of characterization

Crystallization and microstructural evolution of glass powder specimens were examined using several techniques.

Differential thermal analysis was carried out in N_2 atmosphere with platinum sample pans, using a heating rate of 10 °C min^{-1}.

Hot-stage microscopy was carried out in the range 40–1300 °C, with a heating rate of 20 °C min^{-1}.

X-ray diffraction analysis was performed using a graphite monochromatic CuK_α radiation. X-ray patterns were taking by measuring 2θ from 5° to 65° with a step size of 0.02° and a step time of 5 s. The quantitative determination of crystalline and amorphous phase in final glass-ceramic glazes was performed from X-ray diffraction data by using Rietveld refinement. It was performed with Fullprof98 [11], available in the software package Winplotr [12]. The X-ray data were collected from 8° to 100° (2θ) with a step size of 0.02 and a step time of 10 s. The internal standard used was CaF_2. The refinement involved the following parameters: a scale factor, zero displacement correction, unit cell parameters, peak profile parameters using a pseudo-Voight function and overall temperature factor. The structural parameters and atomic positions for mullite [13], spinel [14], rutile [15] and fluorite [16] were taken from the literature.