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Floor tile glass-ceramic glaze for improvement of glaze surface properties

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Abstract

Simultaneous improvement of surface hardness and glossiness of floor tile glaze, without changing its firing temperature, was the main purpose of the present paper. Thus, various glazes in the system of $CaO–MgO–SiO_2–Al_2O_3–ZrO_2$ were prepared and their crystallization behaviors within a fast firing cycle were investigated. With increasing amounts of calcium and magnesium oxides to base glass, the optimum glass-ceramic glaze was obtained. The results showed that with increasing of CaO and MgO part weights in frit, the crystallization peak temperature was gradually decreased and the intensities of diopside and zirconium silicate were increased. The comparison of micro hardness for the optimum glass ceramic glaze derived in this work with a traditional one used in floor tile industries indicates an improvement of 21%. It was found that the glaze hardness not only depend on the amount and type of crystalline phases, but also on the residual glass composition. Furthermore, it was observed that the glaze micro hardness is only slightly affected by thermal expansion mismatch of body and glaze.

Keywords: Glass ceramic; Glaze

1. Introduction

A ceramic floor tile consists of a polycrystalline aluminosilicate substrate and an amorphous opaque glaze layer. The surface hardness of glazed tile (it means surface stability against abrasion, scratching) is one of the main characteristics of a tile which affects on the surface durability, and its beauty.[1] In the traditional opaque glazes used in floor tile industry, opacity usually originates through hardening of glass matrix by addition of a high amounts of opacifiers, e.g. zircon, into the batch.[2] Although the mentioned glazes have a high erosion and abrasion resistance, nowadays the most researches attend to improve the quality of glazes by development of new glaze products with more smooth surfaces and desirable mechanical and chemical properties at the similar firing conditions.[3,4] These new glazes could be available by using the glass ceramic production route.

Glass-ceramics in the $Li_2O–Al_2O_3–SiO_2$, $CaO–MgO–SiO_2–Al_2O_3$ and $ZnO–Al_2O_3–SiO_2$ systems have been investigated for designing of fast firing glazes.[5,6] Among the mentioned systems, the glaze compositions prepared from $CaO–MgO–Al_2O_3–SiO_2$ system mainly consist of inexpensive natural raw materials and are also similar to traditional frits in point of ingredients view.[5,6] The crystalline phases normally precipitate in this system are anorthite ($CaO–Al_2O_3–2SiO_2$), cordierite ($2MgO–2Al_2O_3–5SiO_2$), mullite ($3Al_2O_3–2SiO_2$) and diopside ($CaO–MgO–2SiO_2$). The existence of these crystalline phases increase the micro hardness of glaze surface. Therefore, as we are able to precipitate micro or even submicron particles homogeneously in the glass matrix, by using suitable nucleating agent and cooling procedure the, chance for obtaining harder and more glossy glaze surface will be more with substitution the traditional raw glaze composition by the glass ceramic production one.

2. Experimental procedure

The raw materials used for preparation of the glazes were silica, zircon, kaolin, feldspar, dolomite, magnesium carbonate, boric acid and potassium nitrate in industrial grade. The weighed

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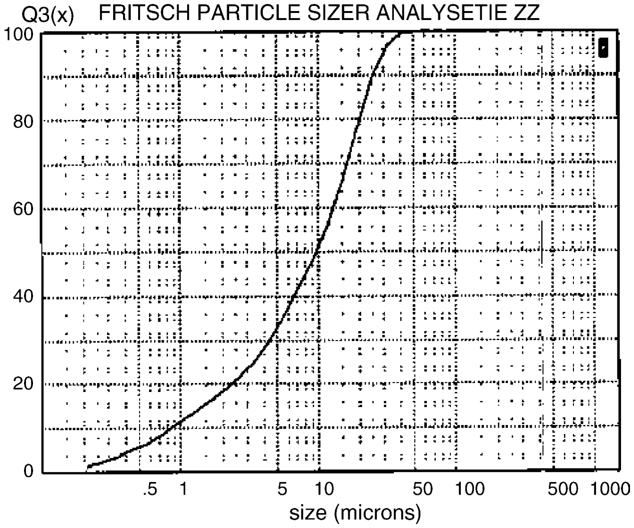

Fig. 1. Particle size distribution of glaze slip.

batch materials, after thorough mixing were melted in an alumina crucible in an electric furnace at 1450 °C for 1 h. The melt was quenched by pouring into water to obtain a glassy frit. The glaze slips were consisted of 93 parts by weight frit, 7 parts by weight kaolin (WBB) and 57 parts by weight water. The batches were fast-milled for 30 min by a planetary mill. A typical particle size distribution of prepared glaze slips, which has been measured by Fritsch Particle Size Analysis, analysette 22 are shown in Fig. 1. The particle size distribution of all glaze slips was almost similar to this analysis. The glazes were applied on 5 cm × 5 cm dried floor tile bodies. The glazed bodies were then dried for 24 h and fired at 1180 °C for 10 min according to a fast firing program in a laboratory electric kiln.

Crystalline phases which were formed in glazes during firing detected by an X-ray diffractometer (Siemens, model D-500) with Cu Kα radiation. Silicon powder was also used as the standard material for semi-quantitative measurements of precipitated phases. A Vickers microhardness tester with a diamond pyramid (MVK-H21 Microhardness) was used to measure the micro hardness of glaze surface by applying a load of 100 g for 30 s. Thermal expansion coefficients of body and glaze was measured by dilatometer (Netzch, E402). The microstructure and the crystallinity of glazes were inspected using a Scanning Electron Microscope (Lika Cambridge Stereoscan 30).

3. Results and discussions

Table 1 shows the chemical analysis of investigated batches compositions. In each compound the letters B, C and M refer, respectively to the base glass, calcium and magnesium oxides and the numbers means the amounts of CaO and MgO, which had been added equally in to the base composition. The primary glass composition was chosen by consideration of floor tile firing schedules and also by precipitation of about 40 wt.% of stoichiometric diopside.

Table 1
Chemical analysis of glasses (parts by weight)

Composition	SiO_2	Al_2O_3	MgO + CaO	ZrO_2	$K_2O + Na_2O$	B_2O_3
B	55.35	8.32	18.57	9.54	3.64	5.58
B-CM5	55.35	8.32	23.57	9.54	3.64	5.58
B-CM10	55.35	8.32	28.57	9.54	3.64	5.58
B-CM15	55.35	8.32	33.57	9.54	3.64	5.58

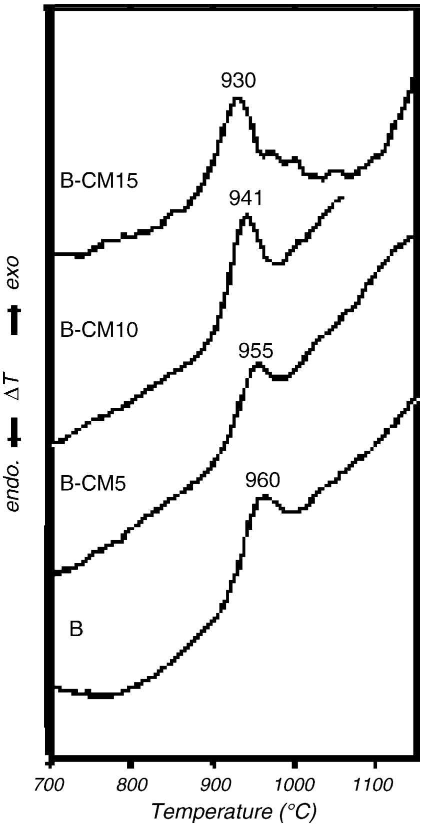

Fig. 2. DTA curves of base glass B, B-CM5, B-CM10 and B-CM15.

Fig. 2 shows the DTA traces of the various glasses. As it can be seen the crystallization, which occurs in the base glass at 960 °C decreased gradually to 930 C with increasing of CaO and MgO amounts. X-ray diffraction (XRD) results of the heat-treated glasses showed that the DTA crystallization peaks belong to precipitation of diopside. X-ray diffraction patterns showed that zirconium silicate was also precipitated during heating program and firing the glazes at 1180 °C (Fig. 3). It seems that zirconium silicate is formed gradually afterwards,in a vast temperature interval of $T_c - T_m$, Where T_c and T_m means the crystallization and maturing temperatures of the glazes, respectively. As bulk crystallization of diopside needs a mixture of nucleating agents, e.g. Cr_2O_3, Fe_2O_3 and TiO_2,[7] it seems, as we expected, surface crystallization was the governor mechanism of crystallization in this work. Reduction of crystallization peak temperature gradually in glasses with increasing of their calcium and magnesium oxides means the improvement of crystallization ability due to decreasing of diffusion paths of crystallite constituents. It is clear that concentration of zirconium ions should be decreased with increasing of CaO and MgO amounts. Therefore, the diffusion ability of $ZrSiO_4$ constituents is diminished and the crystallization ability of zircon is reduced with CaO and MgO. The

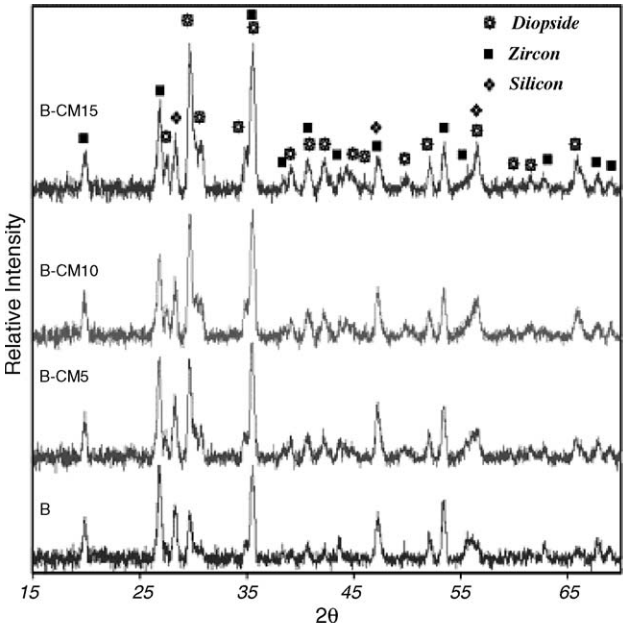

Fig. 3. XRD patterns of base glass B and B-CM5, B-CM10 and B-CM15 compositions after heat-treatment at 1180 °C for 10 min.

intensity ratio of the noted phases to silicon is shown in Table 2. According to these results and in point of crystallization ability view, it was expected that the B-CM15 be more desirable compound. However, as extensive crystallization can retards or even prevents viscous flow of the residual glassy phase, its texture was unfavorably unfired. On contrary to B-CM15 composition, the other glazes had a completely fired texture with a white and smooth surface. Therefore, as melting point of glazes decrease with the number of ingredient oxides,[8] addition of 2.5 parts by weight of zinc oxide to B-CM15 composition was considered. This composition was named B-CM15Z2.5. It should be noted that the use of ZnO is common in glaze industry and its low amounts makes the glaze surface glossier.

Figs. 4 and 5 show the DTA trends and X-ray diffraction patterns of B-CM15Z2.5 and B-CM15 compositions, respectively. It is observed that while the addition of zinc oxide to the glaze did not change the crystallization peak temperature of the glaze, the intensity ratio of precipitated diopside and zircon to silicon after firing the glazes at1180 °C were decreased from 3.75 to 2.32 and 1.04 to 0.9, respectively. Therefore, it seems that the addition of ZnO to the glaze leads to dissolution of diopside into the residual glass phase during firing.

The Vickers micro-hardness of the prepared glass ceramic glazes and a traditional opaque glaze used in floor tile industry are shown in Table 3. For evaluation the effect of thermal expansion mismatch of body and glaze on glaze micro hardness, the Vickers micro hardness was measured at two different conditions, as a coating and as a monolayer specimen. The thermal expansion coefficients of body and glaze B-CM15Z2.5 (in 25–400 °C) were 7.76×10^{-6}/°C and 6.65×10^{-6}/°C, respectively. According to above mentioned results, it can be concluded that in addition of a better surface quality, the prepared glazes possess higher hardness than the traditional floor tile (about 21%), and the residual compression stresses, derives from thermal expansion coefficients mismatch between body and glazes, can just slightly influences on the surface hardness of glaze layer. Furthermore, the comparison of the Vickers micro-hardness of different glazes shows that apart from B-CM15Z2.5, the micro-hardness of other glazes is nearly the same. It is found that various parameters such as porosity, amount and kind of crystalline phases, microstructure and also composition of residual glassy phase can affect the micro-hardness of a glass-ceramic

Table 2
The ratio intensity of diopside peak [2 2 1] and zircon peak [3 1 2] to silicon for prepared glazes

Composition intensity	B	B-CM5	B-CM10	B-CM15
$I_{\text{Diopside}}/I_{\text{Silicon}}$	1.12	2.23	2.27	3.57
$I_{\text{Zircon}}/I_{\text{Silicon}}$	1.28	1.18	0.84	1.04

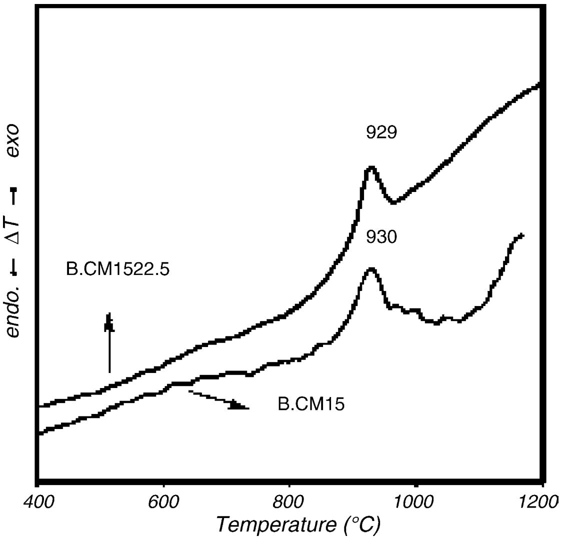

Fig. 4. DTA curve of B-CM15 and B-CM15Z2.5 glasses.

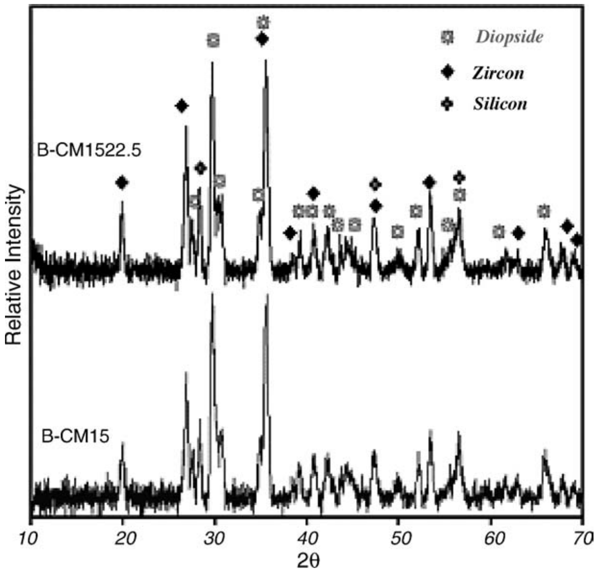

Fig. 5. XRD patterns of B-CM15 and B-CM15Z2.5 glazes after firing at 1180 °C.

Table 3
Vickers micro-hardness of prepared samples and a traditional unfritted one

Composition	B	B-CM5	B-CM10	B-CM15Z2.5	A floor tile unfritted glaze
Micro-hardness as a coating layer (VHN)	649 ± 8	621 ± 2.5	614 ± 5	732 ± 4.5	600
Micro-hardness as a mono-layer (VHN)	624 ± 12.5	614 ± 3.2	610 ± 13.7	717 ± 8.8	–

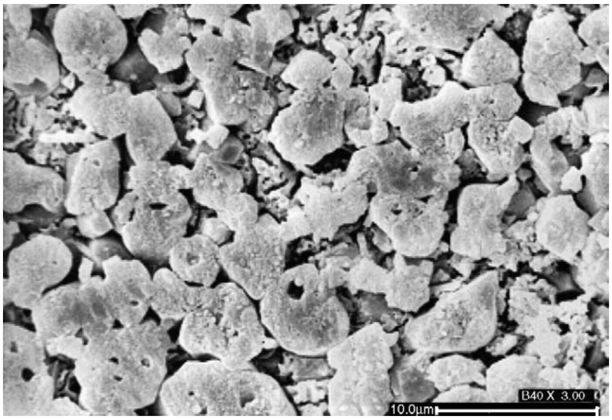

Fig. 6. SEM microstructure of B-CM15Z2.5 glass ceramic glaze.

glaze.[9] As already mentioned, the amount of diopside presented in the specimens decreased with addition of ZnO. This leads to improvement in flow ability of the residual glass phase and thus a better glossy texture of the glaze, which is associates with decreasing of glass ceramic porosity and also enrichment of the residual glass phase with the yields of diopside dissociation. It seems these events could impart in improvement of glaze micro hardness. Fig. 6 shows the SEM microstructure of glaze (B-CM15Z2.5) after firing at 1180 °C for 10 min. The microstructure confirms considerable crystallization of the glaze during fast firing cycle and consisted of minor needle-like and major irregular shape crystalline particles. The EDAX analysis showed that the composition of major phase is compatible with diopside (Fig. 7). The size of needle-like particles were too small to analyzed correctly, however according to XRD results it seems to be zirconium silicate particles.

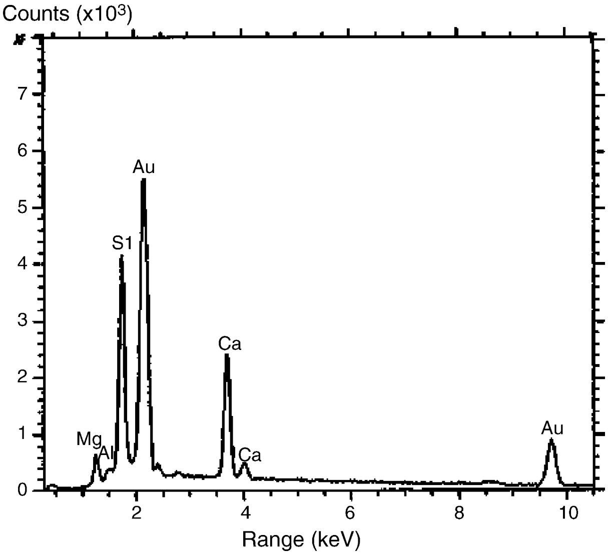

Fig. 7. EDAX analysis of spherical crystals.

4. Conclusions

The investigation showed that although gradual addition of CaO and MgO to the base glaze increases the crystallinity of diopside, however causes an unfired glaze surface. Addition a little amount of ZnO to this high bearing CaO and MgO glaze decreases the crystallinity of it through solution of crystalline phases and improves smoothness of glaze surfaces.

The prepared glass ceramic glaze had a higher micro hardness and also a better surface quality than the traditional glaze, which was used in floor tile industry.

Vickers micro-hardness of glass ceramic glaze not only depends on the type and amount of crystalline phases, but also on the composition of residual glassy phase and porosity of the glaze surface.

Diopside is crystallized as semi-spherical and zircon as needle-like particles. According to our results while diopside is crystallized at about 950 °C, crystallization of zirconium silicate started at higher temperatures and increases continuously up to 1180 °C.

References

1. Esposito, L., Generall, P., Tucci, A. and Nuzziello, S., Hardness of glazed ceramic tiles: comparison between mohs hardness and vickers indentation method. *Ceram. Acta*, 1993, **5**(4–5), 13–21.
2. Romero, M., Rincon, J. M. and Acosta, A., Crystallization of a zirconium-based glaze for ceramic tile coating. *J. Eur. Ceram. Soc.*, 2003, **23**, 1629–1635.
3. Romero, M., Rincon, J. M. and Acosta, A., Effect of iron oxide content on the crystallization of a diopside glass-ceramic glaze. *J. Eur. Ceram. Soc.*, 2002, **22**, 883–890.
4. Torres, F. J. and Alarcon, J., Micro structural evolution in fast-heated cordierite-based glass-ceramic glazes for ceramic tile. *J. Am. Ceram. Soc.*, 2004, **87**(7), 1227–1232.
5. Manfredini, T., Ceramic tile glazes: design, trends and applications. In *Euro Ceramics VII: Proceeding of the 7th Conference Exhibition of the European Ceramic Society*, ed. Erian, Armanios. Trans Tech Publication, Hampshire, 2002, pp. 2031–2034.
6. Babieri, L., Corradi, A., Leoneli, C. and Manfredini, T., Glass-ceramic as tile glazes. In *Glass-ceramic materials fundamentals and applications series of monographs on materials science engineering and technology*, ed. T. Manfredini, G. C. Pellacani and J. M. Rincon. Mucchi Editore, Modena, Italy, 1997, pp. 201–211.
7. Rezvani, M., Eftekhari Yekta, B., Solati-Hashjin, M. and Marghussian, V. K., Effect of Cr_2O_3, Fe_2O_3 and TiO_2 nucleants on the crystallization behavior of SiO_2—Al_2O_3—CaO—MgO (R_2O) glass-ceramics. *Ceram. Int.*, 2005, **31**, 75–80.
8. Singer, F. and Singer, S., *Industrial Ceramics*. Chapman and Hall, London, 1978, p. 534.
9. Escardino Benlloch, A., Crystalline glazes. *Ceram. Acta*, 1996, **8**, 5–35.