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Floor tile glass-ceramic glaze for improvement of the resistance to surface abrasion

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Abstract. The results of research aimed at the study on frits and glass-ceramic glazes for floor tiles, based on compositions located in the primary field of cordierite crystallization within the system $MgO–Al_2O_3–SiO_2$, have been presented.
The results comprise investigations on the frits crystallization abilities, stability of the crystallizing phase under conditions of single-stage a fast firing cycle (time below 60 minutes) depending on their chemical composition and the influence of the nucleation agents. The influence of the nucleating agents namely TiO_2, ZrO_2, V_2O_5 on phase composition of obtained crystalline glazes, mechanical parameters and microstructure, has been examined.
The strength tests proved increased mechanical resistance of crystalline glazes. Obtained glazes are characterized by high microhardness in range 6~8 GPa, as well as the increased wear resistance measured by the loss of weight below 100 mg / 55 cm^2 (PN-EN ISO 10545-7). Significant increase of these parameters as compared with non-crystalline glazes, where micro-hardness values range between 5~6 GPa and the wear resistance values range from 120 to 200 mg, has been proved.
Starting glasses (frits) and glazes of the ternary system $MgO-SiO_2-Al_2O_3$, were examined with use of DTA, XRD and SEM methods.

1. Introduction

Durability, including resistance to scratch and abrasion, is a major parameter of glazes used in floor tile production. Crystallization of glazes is one of the solutions for improving mechanical parameters, with no necessity of greater changes during a firing process. Controlled crystallization of glazes is the most efficient and economic solution used to obtain high quality, mechanically resistant coatings on floor tiles.

Obtaining of frits being devitrified in short time period resulting from modern fast firing technology is a major problem of the glass-ceramic glaze manufacturing process. That means that the processes of crystals nucleation and their growth must interfere (single-phase course) in contradiction to classic technology aimed at obtaining devitrified materials from glass masses. Transformation of frits taking place during very short period of ceramic tiles firing results in obtaining material comprising one or several crystalline phases of high hardness and microhardness. However, properties of the same glazes obtained in devitrification process can be changed depending on qualitative fraction of crystalline and glassy phase. That allows either optimization of their properties or obtaining glazes satisfying various requirements.

2. Experimental procedure

The batches for frits production were prepared with the use of chemically pure components derived from POCh Company in Gliwice, in form of MgO, $CaCO_3$, SiO_2, Al_2O_3, TiO_2, V_2O_5, ZrO_2. The tested compositions of frits are collected in Table 1.

The batches were melted at 1550 ^{O}C being kept at the maximum temperature for 3 hours, and then the melt was quenched by pouring into water to obtain glass frits. The frits were grinded in wet state up to residue of 0~0.1% on sieve 63µm. The grinded frits were dried and then the DTA tests were performed.

Glaze sets containing tested frit and non-crystalline industrial frit FPT-9005 manufactured by quimiCer® Company, have been prepared. Frit FPT-9005 was added to obtain a smooth surface of the glazes. Fraction of auxiliary frit FPT-9005 in the glaze sets was selected experimentally and ranged from 20 to 45% in weight (see Table 3).

Table 1. Chemical compositions of the frits (wt.%).

No.frit Oxide	B-1	B-2	B-3	B-4	T-1	T-2	T-3	T-4	V-1	V-2	V-3	V-4	Z-1	Z-2	Z-3	Z-4
Al_2O_3	25.0	25.0	25,0	30.0	24.0	24.0	24.0	28.8	24.0	24.0	24.0	28.8	24.0	24.0	24.0	28.8
SiO_2	60.0	55.0	50.0	50.0	57.6	52.8	48.0	48.0	57.6	52.8	48.0	48.0	57.6	52.8	48.0	48.0
MgO	15.0	20.0	25.0	20.0	14.4	19.2	24.0	19.2	14.4	19.2	24.0	19.2	14.4	19.2	24.0	19.2
TiO_2	-	-	-	-	4.0	4.0	4.0	4.0	-	-	-	-	-	-	-	-
V_2O_5	-	-	-	-	-	-	-	-	4.0	4.0	4.0	4.0	-	-	-	-
ZrO_2	-	-	-	-	-	-	-	-	-	-	-	-	4.0	4.0	4.0	4.0

The glazes were milled in a ball mill to residue of about 3% on 40 μm sieve. Aqueous suspensions of glazes with the density of 1.65 g/cm^3 were sprayed onto angobe-covered 110x110 mm floor tiles. The glazed tiles were fired in laboratory kiln at 1200^{O}C for 55 minutes (heating-cooling), being kept for 4 minutes at maximum temperature.

To examine microstructure (SEM) and phase composition (XRD) of the glass-ceramic glazes the specimens were etched in 2.5 % HF for a period of 2 minutes. Microhardness HV was determined with the use of indenter under loading of 50 gf. The abrasion resistance has been determined according to the PN-EN ISO 10545-7 standard and the assessment was made on the basis of the mass loss after 6000 rotations of the abrasive material of the surface area of 55 cm^2.

3. Results and discussion

3.1. DTA tests aimed at crystallization of frits

Results of DTA tests are shown in Figure 1. Differences of temperatures of the exothermic peaks with reference to exothermic peak of the frits without nucleators are shown in Table 2.

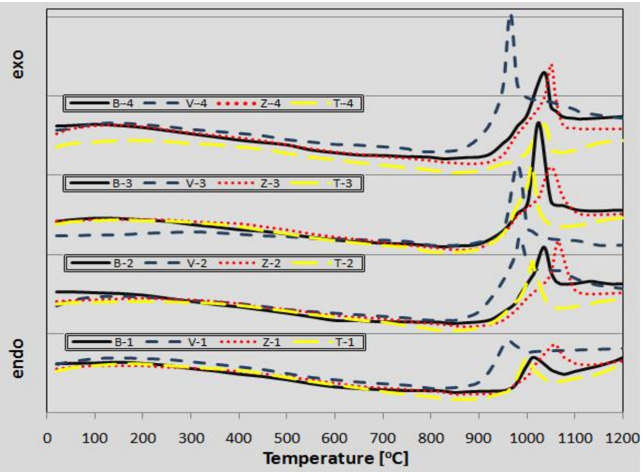

Figure 1. Differential thermal analysis of frits, (heating rate 15^{O}C/min).

Table 2. Temperatures of exothermic peaks [^{O}C].

No. frits	Frits B	T	Z	V
1	1015	1000 (-15)	1060 (+45)	960 (-55)
2	1035	1010 (-25)	1065 (+30)	985 (-50)
3	1025	1010 (-15)	1050 (+25	980 (-45)
4	1035	1035 (0)	1050 (+15)	965 (-70)

B- without nucleating agent,
T - with TiO_2, Z - with ZrO_2, V – with V_2O_5

DTA curves of tested frits proved their crystallization ability within the temperature range from 960 ^{O}C to 1065 ^{O}C. It is preceded by the transformation stage in point T_g at temperature below by about 200 ^{O}C. Shifting of the exothermic peaks toward higher temperatures as a result of Al_2O_3 and/or MgO increased content is observed. It can be related to increase of the viscosity of melts. An addition of nucleators influences on increasing or decreasing the temperatures of crystallization compared to frits without nucleators. Lowering of temperature of exothermic peak by 70^{O}C is particularly observed in case of V_2O_5 nucleator. Addition of TiO_2, depending on oxide composition of frits, can result in slight lowering of the temperature of exothermic peak, whereas ZrO_2 influences temperature increase by 45 ^{O}C.

3.2. Determination of phase composition of glazes (XRD) and SEM microscope observations

The results of analysis in relation to composition of the glazes are shown in Table 3.

Table 3. Composition of the glazes and phases identified after heat treatment.

No.	Glaze							
	GB	GT	GZ	GV	GB	GT	GZ	GV
1	70 / 30	70 / 30	75 / 25	75 / 25	*c*	*c,s*	*c,s*	*c,s*
2	55 / 45	70 / 30	65 / 35	75 / 25	*c, e, s*	*e,s*	*c, e, s*	*c, e, s*
3	55 / 45	65 / 35	60 / 40	55 / 45	*c,e*	*e,s*	*e,s*	*c, e, s*
4	55 / 45	60 / 40	60 / 40	60 / 40	*c, e, s*	*e,s*	*c, e, s*	*c, e, s*

A / B – A- fraction of crystalline frit, B – fraction of non-crystalline FTP 9005 frit
c-cordierite $Mg_2Al_4Si_5O_{18}$, *s-spinel* $MgAl_2O_4$, *e-enstatite* $Mg_2[Si_2O_6]$

The SEM images of glazes are shown in Figure 2.

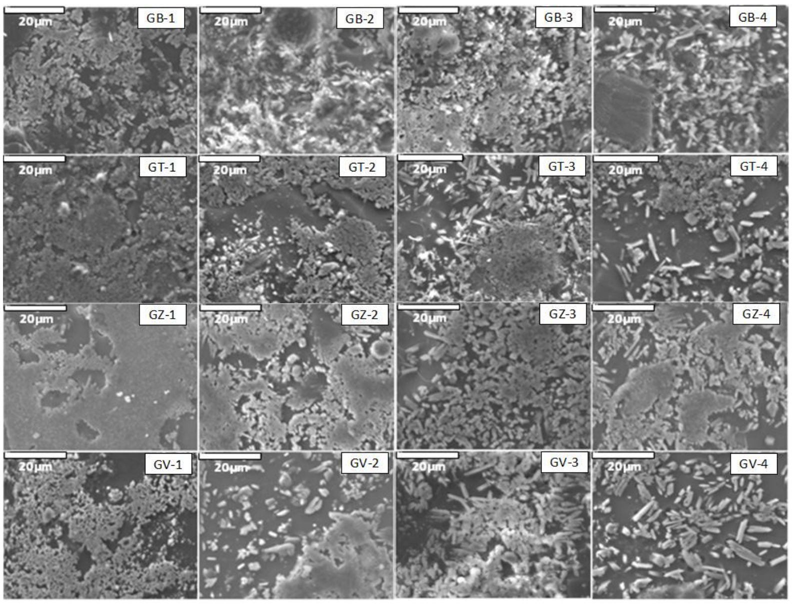

Figure 2. SEM microphotographs (x5000).

Packed bar-shaped and/or needle-shaped grains of grain-size of 15 µm and isometric grain having dimensions of several micrometers are observed on SEM images of the specimen morphology.

The presence of nucleators TiO_2 and V_2O_5 had distinct influence in case of glazes No.3 and No.4 to form needle-shaped grains. Visible influence on development of bigger amount of finer grains in each series of tested glazes (GZ-1, GZ-2, GZ-3, GZ-4), during crystallization, was observed in case of ZrO_2.

3.3. Measurement of the microhardness (HV) and evaluation of abrasion resistance

The testing results are shown in Table 4. Microhardness was differing in individual glaze series within the range from 6.40 to 7.83 GPa, and its values are higher than microhardness of traditional non-crystalline glazes ranging within the limits 5.2~6.4 GPa [1, 2, 3, 4, 5]. In glazes No. 2 and No. 3 in the presence of nucleators an increase of microhardness was observed. The strongest effect in those glazes was found when TiO_2 was used.

Table 4. Microhardnes HV and abrasion resistance of glass-ceramic glazes.

Glaze No.	GB	GT	GZ	GV	GB	GT	GZ	GV
	HV [GPa]				Weight losses (6000rpm)[mg]			
1	*7.15 ± 0.19*	*6.88 ± 0.28*	*6.59 ± 0.12*	*6.90 ± 0.25*	*59 ± 2*	*62 ± 7*	*56 ± 9*	*63 ± 8*
2	*6.69 ± 0.33*	*7,26 ± 0.19*	*7.18 ± 0.30*	*7.09 ± 0.54*	*69 ± 8*	*53 ± 3*	*62 ± 8*	*54 ± 5*
3	*6.86 ± 0.84*	*7.52 ± 0.43*	*7.05 ± 0.55*	*7.04 ± 0.29*	*54 ± 3*	*54 ± 7*	*65 ± 2*	*58 ± 5*
4	*7.83 ± 0.80*	*7.06 ± 0.25*	*6.97 ± 0.53*	*6.40 ± 0.39*	*77 ± 10*	*70 ± 6*	*68 ± 3*	*82 ± 7*

Glaze contains 100% non-crystalline FPT-9005: HV =5.42 ± 0.27GPa, weight losses = 160 mg

Mass losses of tested glazes determined for 8 specimens are shown in Table 4. All tested glazes are characterized by increased abrasion resistance with relation to non-crystalline glazes. The mass losses ranged from 53 to 82 mg, whereas for traditional, non-crystalline glazes, these values range from about 120 to 200 mg [1]. The effect of nucleators on abrasion resistance of tested glazes depends on initial sets of glazes, for instance ZrO_2 is effective in glazes No.1 and No.2, TiO_2 in glazes No.2 and No.4, V_2O_5 in glaze No.2.

No dependence was observed between the type of used nucleators and obtained crystalline phases in tested glazes. However, in the SEM microphotographs of the samples of the glazes different amounts of crystalline phases and residual glass were observed.

4. Conclusions

Compositions of frits which were designed and tested are located in the primary field of cordierite crystallization within the $MgO–Al_2O_3–SiO_2$ system and can be successfully used as constituents of floor tile glazes.

Glazes obtained on the basis of designed frits crystallize in a fast firing cycles, forming glass-crystalline composites.

The presence of nucleators, namely: TiO_2, ZrO_2, V_2O_5 used at amount of 4% in weight influences on different amounts and shape of crystalline phases and residual glass, as well on shift of crystallization exothermic effect on DTA curves.

The presence of crystalline phases of cordierite, enstatite and spinel in tested glass-crystalline glazes has decisive influence on the increase in microhardness and abrasion resistance with relation to non-crystalline glazes.

Among the tested glazes, glaze No. 3 with the nucleator TiO_2 was of the highest microhardness (7.52 GPa) and also the highest abrasive resistance (54 mg).

5. References

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