COMPARISON OF GLASS-CRYSTALLINE GLAZES OBTAINED IN THE LABORATORY AND INDUSTRIAL APPLICATIONS

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ABSTRACT

Glass-crystalline glazes with improved mechanical properties, prepared and obtained in the laboratory, were compared with identical glazes fired in industrial conditions. The tested glazes for floor tiles were based on compositions located in the primary field of diopside crystallization within the system CaO-MgO-Al_2O_3-SiO_2. The results obtained from a sample of the industrial glazes are very similar to those for glazes obtained in the laboratory conditions, particularly in terms of their high abrasion resistance.

Experimental glazes are characterized by high microhardness in the range of 6 ~ 7 GPa, as well as the increased wear resistance measured by the loss of weight below 100 mg/55 cm^2 (ISO 10545-7). A significant increase of these parameters, compared with non-crystalline glazes, where microhardness values were in the range between 5 ~ 6 GPa and the wear resistance values were in the range from 120 to 200 mg, was verified.

Starting glasses (frits) and glazes of the system CaO-MgO-Al_2O_3-SiO_2 were examined with use of DTA, XRD and SEM methods.

1. INTRODUCTION

One of the major parameters of floor tile glazes is their durability, including scratch resistance and wear resistance. A method that makes it possible to enhance the mechanical parameters without having to make any substantial changes to the firing cycle is by crystallization of the glazes. The controlled crystallization of glazes has proved to be the most effective and most economical way of obtaining high-quality mechanically resistant floor tile coatings.

The basic problem in producing glass-crystalline glazes is to obtain frits (glasses) that will undergo devitrification in the short time imposed by the existing fast-firing technology. This means that the nucleation and crystal growth processes will have to overlap, and thus to proceed in a single stage, in contrast to the classical technology of producing devitrification materials from molten glasses. Thanks to the transformation of frits (glazes) occurring during the very short time of firing ceramic tiles, a material is obtained, which contains one or several crystalline phases of high hardness and microhardness. However, the properties of the glaze itself as obtained in the devitrification process may vary, depending on the quantitative fractions of the crystalline and vitreous phases. This opens possibilities for optimizing their properties or producing glasses meeting various requirements.

Another problem in obtaining glass-crystalline glazes, though not only glazes, is to transfer their production technology from the laboratory conditions to the industrial conditions. It is a well-known fact that technologists are not always successful in scaling up, and it often happens that very good glazes obtained in smaller samples must be additionally modified or even rejected when it is attempted to implement them in series production. An important element in laboratory studies on new solutions is their testing under industrial conditions, which is the aim of the present study.

This study is a continuation of research on glass-crystalline glazes from the $MgO–Al_2O_3–SiO_2$ system. For the purposes of the present study, glaze compositions were selected, which offered the best chances for obtaining the best results [1].

2. EXPERIMENTAL

The batches for frit 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.

Frit ref. Oxide	FB	FT	FV	FZ
Al_2O_3	10.0	9.6	9.6	9.6
SiO_2	55.0	52.8	52.8	52.8
MgO	10.0	9.6	9.6	9.6
CaO	25.0	24.0	24.0	24.0
TiO_2	–	4.0	–	–
V_2O_5	–	–	4.0	–
ZrO_2	–	–	–	4.0

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

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 a sieve of 63μm. The ground 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, were 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.

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 engobe-covered 110x110 mm floor tiles. Glazed tiles were fired in a commercial roller furnace supplied by SACMI for 34 minutes at a maximum firing temperature of 1194°C, along the firing curve close to the one used in the laboratory conditions.

The fired tiles were subjected to microhardness (HV) tests and abrasion tests by measuring the loss of mass after 6000 revolutions under the abrasive load conforming to the PN-EN ISO 10545-7 standard. The phase composition determination (XRD) and microstructure observation (SEM) of glaze surfaces were carried out on the surfaces of glazes that had been etched in 2.5% HF for 2 minutes. The results of the glazes tested were compared with the results obtained on the laboratory scale.

3. RESULTS AND DISCUSSION

DTA tests on frit crystallization

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

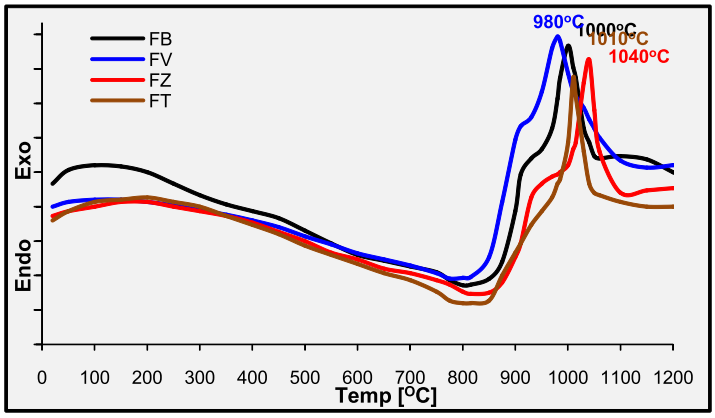

Figure 1. *Differential thermal analysis of frits, heating 15OC/min.*

FB	FT	FZ	FV
1000	1010 (+10)	1040 (+40)	980 (-20)

FB - without nucleating agent,
FT - with TiO_2, FZ - with ZrO_2, FV – with V_2O_5.

Table 2. *Temperatures of exothermic peaks [OC].*

The behaviour of the DTA curves for the frits tested indicates a high tendency to crystallization in the temperature range from 980°C to 1040°C. The DTA curves have a similar shape, with a single sharp exothermic peak which is preceded by the transformation stage at point T_g at a temperature lower by approx. 200°C than that of the crystallization peak. The analysis of the DTA results shows that the addition of 4 wt% of TiO_2 and ZrO_2 has had the effect of increasing the exothermic peak temperature compared to the base frit. The addition of 4 wt% of V_2O_5 has resulted in a reduction in the peak temperature.

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

The results of XRD analyses are in Table 3.

Ref.	Laboratory conditions	Industrial conditions
GB	*diopside* $CaMgSi_2O_6$	*diopside* $CaMgSi_2O_6$
GT	*diopside* $CaMgSi_2O_6$	--------
GZ	*diopside* $CaMgSi_2O_6$	*diopside* $CaMgSi_2O_6$
GV	*diopside* $CaMgSi_2O_6$	*diopside* $CaMgSi_2O_6$

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

In the glazes obtained from the industrial trial, the main crystalline phase is diopside, similarly as in the glazes obtained in the laboratory conditions, which is confirmed by X-ray examination.

Figure 2 shows SEM photographs of glazes obtained in the laboratory conditions (*GB-L, GT-L, GZ-L, GV-L*) and in the industrial conditions (*GB-I, GT-I, GZ-I, GV-I*).

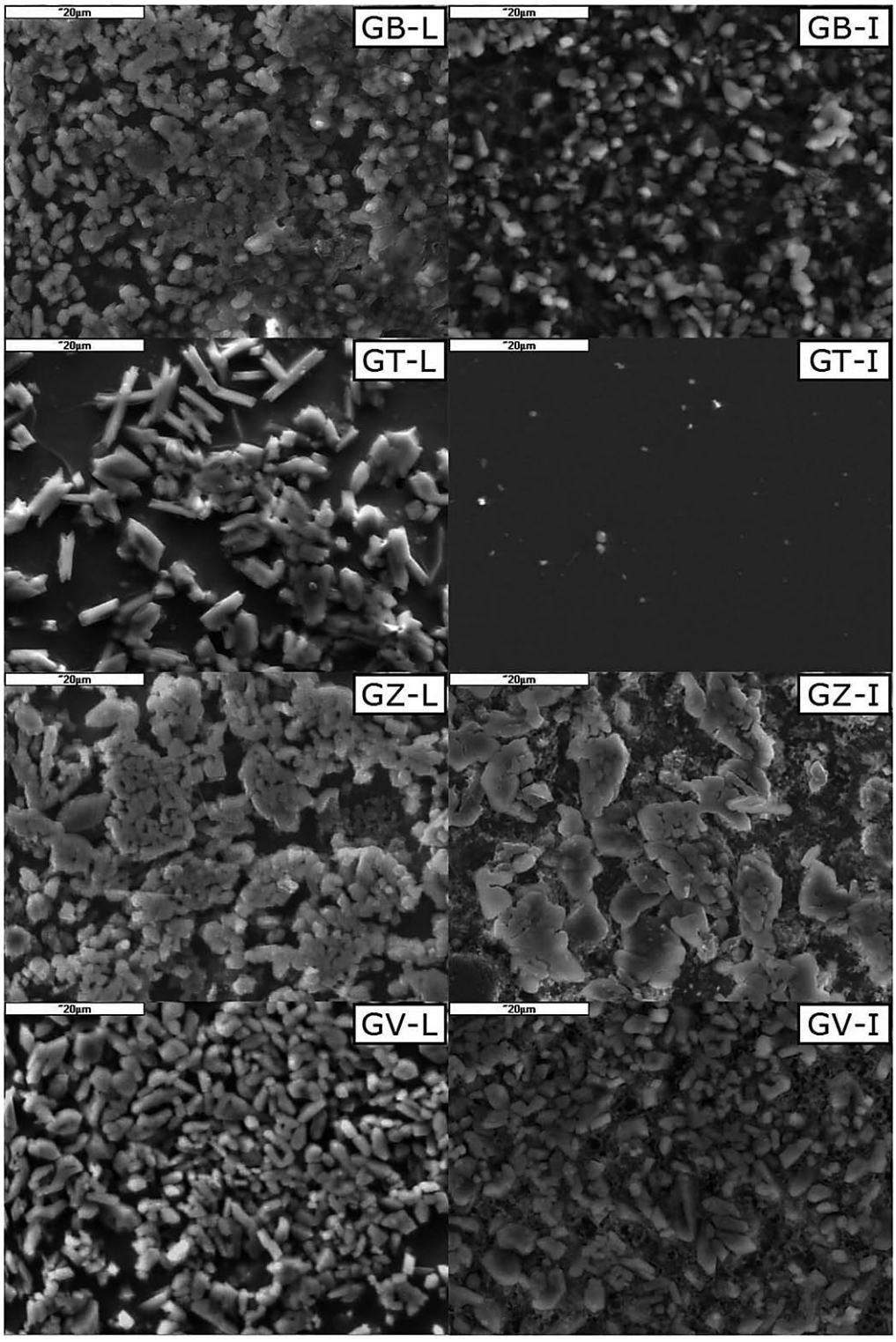

Figure 2. *SEM microphotographs (x5000); glazes obtained in the laboratory conditions GB-L, GT-L, GZ-L, GV-L, glazes obtained in the industrial conditions GB-I, GT-I, GZ-I, GV-I.*

In the glazes obtained in the laboratory conditions without a nucleator *(GB-L)* and with nucleators ZrO_2 *(GZ-L)* and V_2O_5 *(GV-L)*, the crystal habit is chiefly isometric. In these glazes, a close packing of crystals on the entire surface is observed. In the glaze *(GT-L)* with the TiO_2 addition, the crystalline phase has the form of oblong columns not exceeding 10 µm in size, and is much less in quantity.

In analogous glazes obtained under industrial conditions, the crystalline phase has an isometric habit, with the appearance of the glazes being similar to that of the glazes obtained under laboratory conditions. The crystal sizes in the laboratory and industrially obtained glazes are similar, though a certain quantity of smaller size crystals is observed in the glazes *GB-I* and *GV-I*. In the case of the glaze *GT-I* with the TiO_2 addition, no crystals were observed, in contrast to the laboratory test glaze *GT-L*. The absence of the crystalline phase in this glaze can be hypothetically ascribed to the process of the crystalline phases dissolving in the melt, or is due to the fact that the crystallization has not occurred at all.

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

The results of examinations are presented in Table 4.

Ref.	Laboratory conditions		Industrial conditions	
	HV [GPa]	Weight losses (6000rpm) [mg]	HV [GPa]	Weight losses (6000rpm) [mg]
GB	*7.52 ± 0.76*	*42 ± 6*	*6.62 ± 0.43*	*57 ± 3*
GT	*6.58 ± 0.18*	*69 ± 4*	*5.42 ± 0.28*	*131 ± 7*
GZ	*6.87 ± 0.20*	*64 ± 5*	*5.96 ± 0.34*	*69 ± 4*
GV	*7.52 ± 0.57*	*66 ± 8*	*6.63 ± 0.41*	*53 ± 5*

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

The microhardness values of the glazes obtained in the industrial and laboratory conditions are all contained in the range from 5.42 to 7.52 GPa. The glazes obtained under the industrial conditions have microhardness lower than that of the glazes obtained in the laboratory conditions. Nonetheless, in the case of the glazes obtained in the laboratory conditions, these values exceed the microhardness values of traditional non-crystallized glazes, which are in the range of about 5 ~ 6 GPa [2, 3, 4]. The glazes obtained from the laboratory and industrial trials are characterized by high abrasion resistance, as illustrated by low mass losses of about 50 ~ 70 mg. The exception is the TiO_2 addition glaze *GT-I*, whose mass loss is 131 mg, and the microhardness is the lowest, being 5.42 GPa. Such a mass loss classifies this glaze rather to a class of lower abrasion resistant glazes.

4. CONCLUSION

The tests of the $MgO–CaO–Al_2O_3–SiO_2$ system's glass-crystalline glazes under industrial conditions were aimed at determining their properties as against the same composition glazes obtained in the laboratory conditions and establishing the potential for their possible implementation in commercial production.

In the industrial process, glass-crystalline glazes with a diopside crystalline phase were obtained, identically as in the laboratory conditions.

It was found that the glazes obtained under the industrial conditions were characterized by lower microhardness, compared to the ones obtained in the laboratory conditions. In spite of this fact, glazes were obtained, which showed an enhanced abrasion resistance of below 70 mg, compared to traditional non-crystallized glazes. In the case of the glaze *GT-I*, an impairment in abrasion resistance (130 mg) was found. No crystalline phases were found to occur in the glaze *GT-I*, which might have contributed to the impairment in the resistance of this glaze.

In spite of the differences between the industrial and laboratory firing conditions, glazes of a similar microstructure pattern and phase composition were obtained. The *GT-I* glaze case of indicates that variations in firing conditions, with the improper selection of the nucleator, may substantially influence the change in the phase composition.

The results of the study enable one to state that the developed glazes can be applied industrially.

ACKNOWLEDGEMENTS

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