CRYSTALLIZATION BEHAVIOUR OF $CaO-Al_2O_3-SiO_2$ GLASS-CERAMIC GLAZES USING TiO_2 AND MULLITE UNDER FAST FIRING CONDITIONS

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ABSTRACT

This study aimed to investigate the effects of different amounts of TiO_2 and mullite addition on the crystallization behaviour of glass–ceramic glazes belonging to the $CaO–Al_2O_3–SiO_2$ system. For this aim, anorthite-based glass-ceramic glazes were synthesized by formulating TiO_2 or mullite doped glaze compositions containing different frits. Synthesized glazes were applied on to the porcelain tile and fired at 1205ºC in an industrial roller furnace for 42 minutes (cold to cold). The crystalline phases were determined by X-ray diffraction (XRD). Anorthite was found to be the only crystalline phase that exists in the glass-ceramics system. The crystallization kinetics were determined by differential

thermal analysis (DTA). A scanning electron microscope (SEM) attached to an energy dispersive (EDX) spectrometer was further employed to investigate microstructural and microchemical features on the fired glazes. According to the results, anorthite crystallization was improved with the addition of TiO_2 and mullite. However, the presence of lath-like anorthite crystals was observed in the form of segregated regions across the TiO_2 doped glaze. This caused the formation of expansion cracks within the glaze.

1. INTRODUCTION

The surface hardness and the resistance to scratch and abrasion are key characteristics of glazed floor tiles that are constantly subject to wear, which affects surface durability. Glazed ceramic floor tile surfaces rapidly deteriorate, losing gloss especially in the areas of high traffic. Nowadays, most research seeks to improve the quality of glazes by development of new glaze products with abrasion resistance and hardness. These new glazes could be available by using glass-ceramics containing harder crystalline phases as reinforcing elements.

Zircon or zircon-bearing frits are frequently used for the improvement of opacity as well as mechanical properties (mostly wear resistance) in glaze formulations[1,2]. Due to the high market price of zircon, the current tendency is to decrease zircon content and use glass-ceramic systems. The high glaze hardness is required to improve the glaze wear resistance. The ability to precipitate hard crystalline phases, e.g. anorthite ($CaO–Al_2O_3–SiO_2$) with hardness of 6 Mohs, as well as abundant and economical raw materials (e.g. calcium carbonate, kaolin, etc.) make it favourable for different applications such as building glass–ceramics, floor tiles, claddings, etc.[3] The introduction of glass-ceramic composites in which a crystalline phase has a greater hardness could be a solution to raise glaze mechanical properties and hardness. The particle size, shape and the quantity of crystalline reinforcing phase formed at the industrial firing conditions are also a crucial factor for the hardness and wear properties of the glass-ceramic glazes[4].

Anorthite-based glass-ceramics are characterized by high mechanical strength and good chemical durability. Glass compositions that lie in the primary crystallization field of anorthite devitrified easily, but they are not readily internally nucleated5. In the present work, anorthite crystals were chosen as a reinforcing crystalline phase in the glass-ceramic composite glazes. First of all, anorthite-based glass-ceramic glazes were synthesized successfully at the industrial fast firing conditions. Then, the effects of different amounts of TiO_2 and mullite based nucleating agents on crystallization and mechanical properties of glass–ceramics belonging to the $CaO–Al_2O_3–SiO_2$ system were investigated. By the addition of 2 wt% TiO_2, the anorthite phase was formed as clusters.

2. MATERIALS AND METHOD

The suitable glaze compositions in the anorthite primary phase field of the $CaO–Al_2O_3–SiO_2$ were designed by using two different commercial frits. The oxide mole ratio of the studied glaze compositions are given in Table 1. The glazes were formulated with different amounts of TiO_2 and mullite (Table 2). Carboxymethylcellulose (CMC), sodium tripolyphosphate (STPP) and water were mixed and milled in a ball mill to a residue of about 2% on a 63 µm sieve.

The glaze suspensions were applied to green floor tile bodies that had previously been engobed. The dried samples were fired at 1205ºC under industrial fast firing conditions in which the total firing program was 42 min. at Vitra Karo San. Tic. A. S.

The crystalline phases present in the glazes were identified by XRD (Rigaku Rint 2000 series diffractometer with Cu K radiation). The microstructure of the crystallized glaze samples was studied by scanning electron microscopy (SEM, SUPRA 50VP at 20 kV), fitted with an EDX. The colour values L*, a*, and b* of all fired tiles were measured using a Minolta CR-300 series chroma meter. Gloss was determined with a gloss meter (Minolta Gloss 268) with 20º, 60º and 85º light incident angles on the glaze surface. The frit crystallization capability and crystallization temperature range were determined with a simultaneous thermal analyzer (Netzsch, STA 409PG) at a rate of 10 $Kmin^{-1}$. The scratch hardness of surface was determined according to the Mohs scale. The abrasion resistance was determined according to the EN-ISO 1545-7 standard (PEI method) and the assessment was made according to the EN-ISO 14411 standard.

3. RESULTS AND DISCUSSION

The anorthite-based glass-ceramic glaze composition was designed by optimizing the CaO/Al_2O_3 and adjusting the Al_2O_3/alkali ratio in the composition. The Seger formula of the studied glaze in the $CaO-Al_2O_3-SiO_2$ system containing a total of ~16 wt% frit is given in Table 1. The commercially available frits were also added in order to achieve the required fluidity at high temperatures. TiO_2 and mullite were employed as a nucleating agent in the studied glaze compositions (Table 2).

Component	Content (mol %)
R_2O (Na_2O, K_2O)	6.16
RO (CaO, MgO, ZnO)	29.91
R_2O_3 (B_2O_3, Al_2O_3, Fe_2O_3*)	16.02
RO_2 (SiO_2, ZrO_2, TiO_2*)	50.12
Total	100

Table 1. The Seger formula of the investigated glazes.

* Fe_2O_3 and TiO_2 coming from certain raw materials and their amounts are negligible.

	GT-2	GT-5	GM-3	GM-6
Glaze-G	98	95	97	94
TiO_2	2	5	-	-
Mullite	-	-	3	6

Table 2. The formulation of investigated glaze.

The chromatic coordinates and gloss values of the studied glazes fired under industrial conditions are given in Table 3. Although the colour and gloss values of the 5 wt% TiO_2-doped (GT-5) glaze were higher than those of the standard glaze (Glaze-G), it showed undesirable surface quality. High amounts of TiO_2 in the glaze recipe resulted in an increased surface crystallization and caused cracks at the surface most probably due to the thermal expansion mismatch between segregated crystals and glass. The colour values of the mullite-doped glazes were closer to the standard one, but the gloss values decreased with the increasing mullite addition due to the mullite dissolution at high temperatures. According to the industrial firing conditions, the GT-2 glaze has acceptable colour and gloss values, and it also has desirable surface quality.

Glazes	L*	a*	b*	Gloss (20º)	Gloss (60º)	Gloss (85º)
G-Glaze	71.68	0.39	2.86	1.2	5.8	21.3
GT-2	73.75	0.19	2.64	1.3	6.2	25
GT-5	76.38	-0.06	2.49	1.8	8.6	31.2
GM-3	73.81	0.16	2.21	1.2	5.1	20.6
GM-6	74.31	0.11	1.89	0.9	3.9	11.3

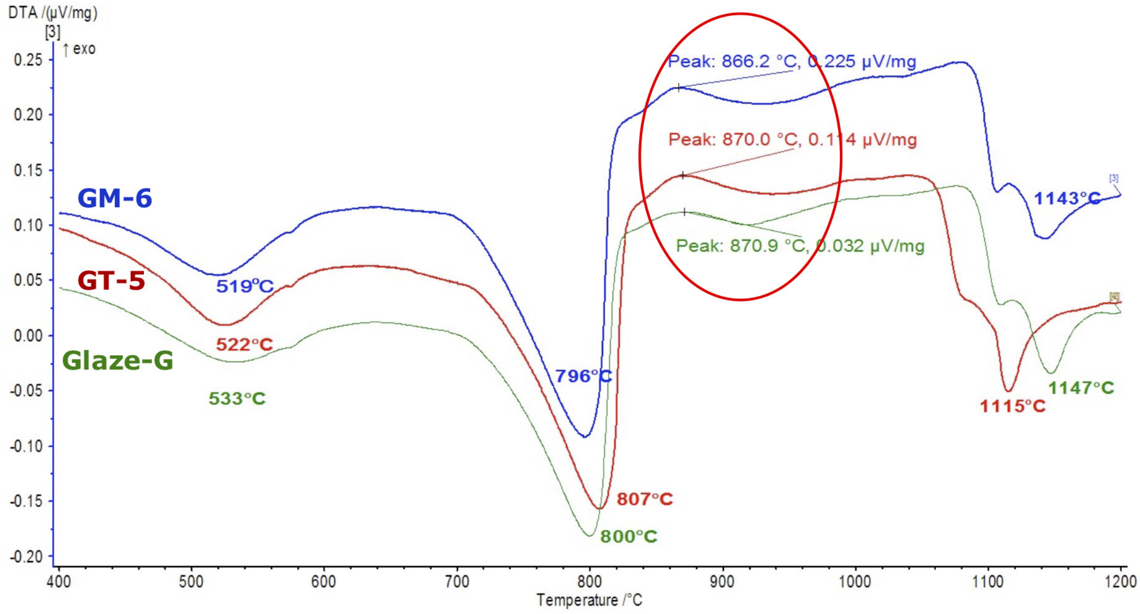
Table 3. Colour (L, a*, b*) and gloss values of the glazes.*

The abrasion resistance, using the PEI-visual evaluation according to the EN-ISO 1545-7 standard test, was applied to investigate the effect of the anorthite as a reinforcing phase. The test results with the assessment according to the EN-ISO 14411 standard are given in Table 4. The required hardness values were achieved with the addition of TiO_2 and mullite. According to the results, GT-2 glaze shows better wear performance although it has a lower hardness value than that of the GT-5, GM-3, and GM-6 glazes.

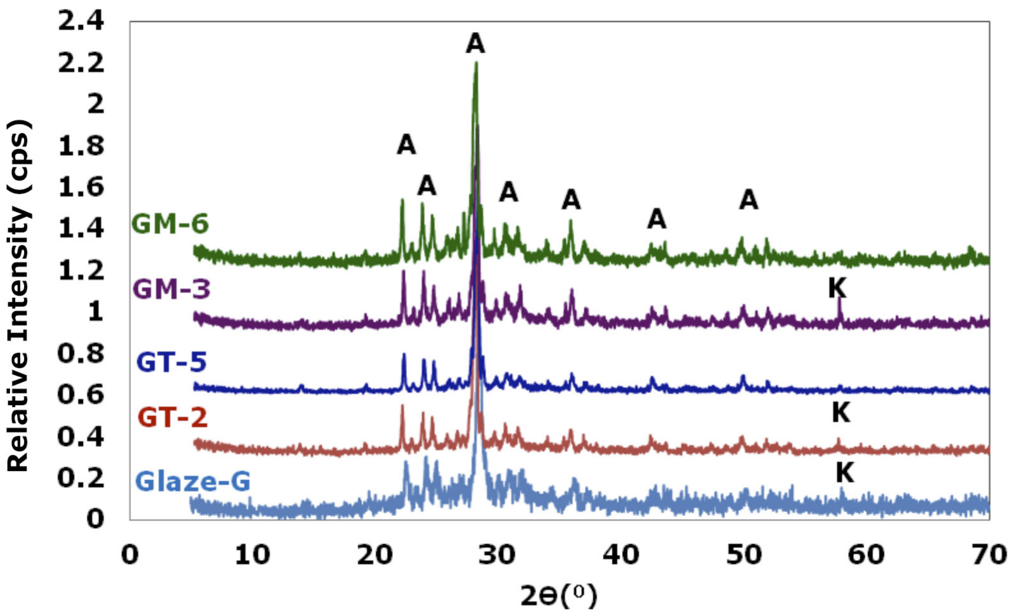
	G	GT-2	GT-5	GM-3	GM-6
Class, PEI	4	5	4	4	4
Mohs hardness	5	6	7	7	9

Table 4. The abrasion resistance (PEI class) and the Mohs hardness class of the samples.

Fig. 1 shows the DTA analysis results of the raw glazes (G, GT-2, GM-6). The endothermic peaks observed at around 520-530ºC and 860-871ºC correspond to the kaolinite and $CaCO_3$ decomposition, respectively. The glazes exhibit exothermic peaks of the same magnitude belonging to the anorthite formation. It is shown that there is no influence of the TiO_2 or mullite addition on crystallization peak temperature, which is around 870ºC. The intensity of the crystallization peak is not sharp since the raw glazes were examined. However, it can be seen that with the addition of 5% TiO_2, the melting temperature of the glaze was reduced to 1115ºC which was around 1145ºC.



The XRD spectra of the original glass-ceramic glazes taken from the fired glazed tile surfaces are given in Fig. 2. It is clearly seen that TiO_2 or mullite addition did not contribute to the formation of any other crystalline phases and anorthite is the only crystalline phase that exists in the glazes with corundum which is employed to the some glaze recipes (GT-5, GM-3, GM-6) at the same amount. The glazes with corundum show greater hardness values (Table 4). The Rietveld method with MAUD (material analysis using diffraction) program was used for the quantitative analysis of the crystalline and amorphous phases present (Table 5). The crystalline/amorphous phase fractions were increased by the addition of TiO_2. Mullite additions do not have any influence on the quantity of the anorthite crystals.

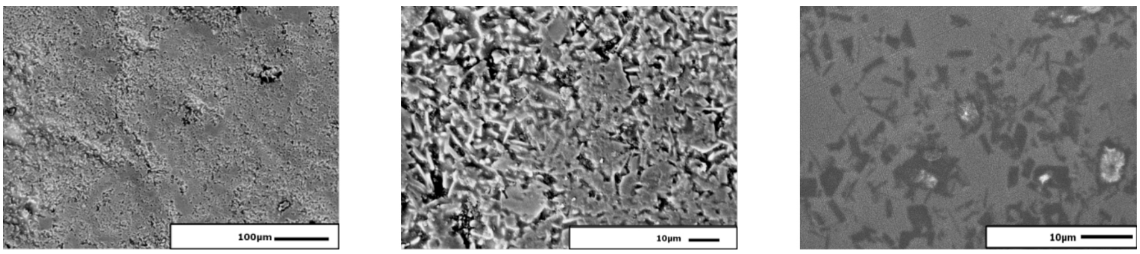


	Anorthite (%)	Amorphous phase (%)	Corundum (%)
Glaze-G	48.22 ± 0.73	51.78 ± 1.31	---
GT-2	66.08 ± 0.78	33.92 ± 1.60	---
GT-5	68.06 ± 0.73	30.11 ± 1.51	1.83 ± 0.14
GM-3	53.65 ± 0.61	43.54 ± 1.55	2.81 ± 0.19
GM-6	48.30 ± 0.80	49.61 ± 1.48	2.08 ± 0.18

Table 5. Quantitative phase analysis of the investigated glazes.

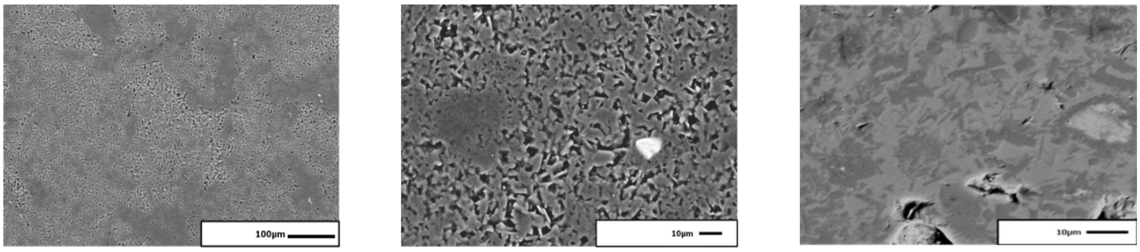
Microstructural studies of the glazes were made on the surface and the cross-section of the specimens. Figs. 3-6 show the micrographs obtained by backscattered electrons of the specimens. The glass-ceramic glaze without any addition of TiO_2 or mullite shows a significant amount of anorthite crystals distributed homogeneously through the surface (Fig. 3). The aesthetic characteristics (colour and gloss) of the glazes were also suitable for industrial production. The anorthite crystallization through the cross-section is however not as high as the surface. There is a strong dependence of the wear rate on the surface hardness and the cross-section of the glass-ceramic microstructure.

It was attempted to increase the quantity of anorthite crystals at the surface and cross-section of the glaze with the addition of TiO_2 as a nucleating agent. The presence of lath-like anorthite crystals was observed in the form of segregated regions through the surface and cross-section of the TiO_2 doped glaze (Figs. 4-6). These segregated crystals are believed to have beneficial effect on wear behaviour. The segregated crystals at the surface and the crystal/amorphous fraction of the glaze were increased by increasing the TiO_2 content. This caused the formation of expansion cracks within the glaze containing 5% TiO_2. The cross-section of the GT-5 seen on Fig. 5 shows these cracks extended from the surface towards the cross-section.



(a) (b) (c)

Fig. 3. SEM micrographs taken from the surface (a,b) and cross-section (c) of glaze-G at different magnifications.



(a) (b) (c)

Fig. 4. SEM micrographs taken from the surface (a,b) and cross-section of glaze GT-2 at different magnifications (1KX, 5KX).

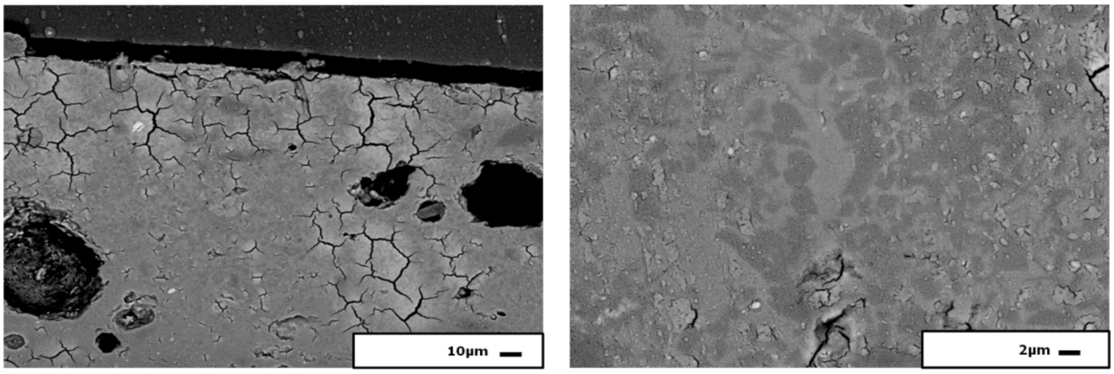


Fig. 5. SEM micrographs taken from the cross-section of glaze GT-5 at different magnifications.

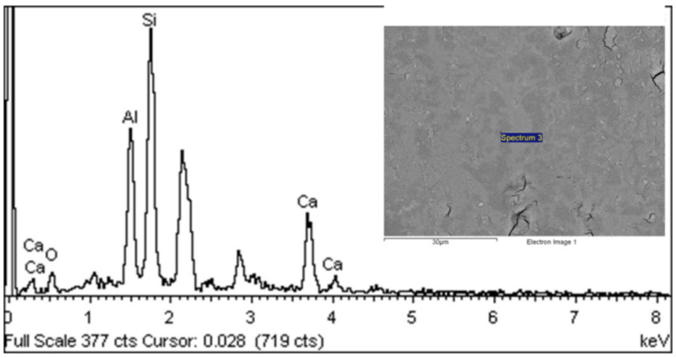
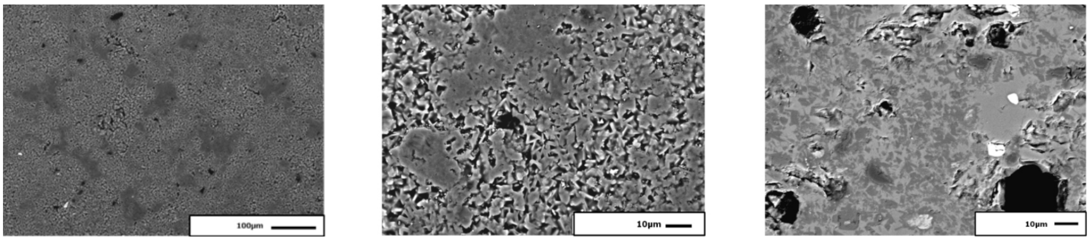


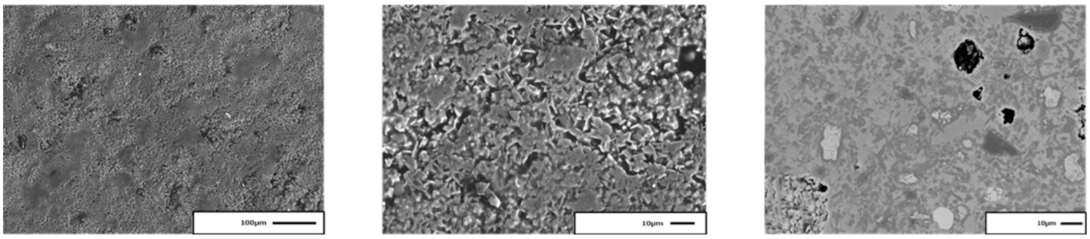
Fig. 6. EDX spectra of the glaze GT-5 presenting anorthite crystallization.

The segregated anorthite crystallization at the surface and the cross-section of the mullite-doped glass-ceramic glaze can also be seen in the SEM images (Figs. 7-9). As observed, crystal size and shape are different than in the glaze-G and TiO_2-doped glazes. The anorthite crystals at the cross-section of the glaze are smaller in size and equiaxed-shaped, which is a disadvantage for the wear properties.



(a) (b) (c)

Fig. 7. SEM micrographs taken from the surface (a,b) and cross-section (c) of glaze GM-3 at different magnifications.



(a) (b) (c)

Fig. 8. SEM micrographs taken from the surface (a,b) and cross-section (c) of glaze GM-6 at different magnifications.

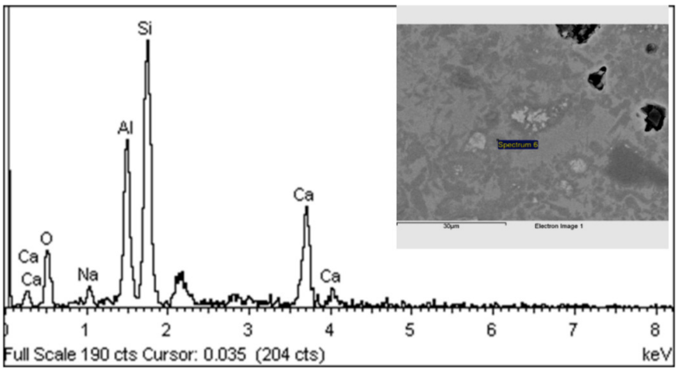


Fig. 9. EDX analysis of glaze GM-6 presenting anorthite crystallization (C, Corundum).

4. CONCLUSIONS

The glaze composition which was designed and developed in the primary field of anorthite crystallization within the $CaO-Al_2O_3-SiO_2$ system was successfully obtained as a floor tile glaze under industrial firing conditions. Microstructural analysis showed that surface crystallization was the dominant mechanism of these glazes.

Although, introduction of 2 wt% TiO_2 did not cause any considerable effect on crystallization peak temperature, it caused further anorthite crystallization at the surface and cross-section of the glaze. This increase is believed to be the reason for improved wear behaviour.

The introduction of a glass-ceramic composite in which a crystalline phase has a greater hardness is an effective approach, but it is not the only parameter that has to be considered. The particle size, shape and quantity of crystalline reinforcing phase formed at the industrial firing conditions are also crucial factors for the wear properties of glass-ceramic glazes.

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