

## KINETIC STUDY OF THE CRYSTALLIZATION PROCESSES OF SOME DECORATIVE CERAMIC GLAZES

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A kinetic study of the crystallization processes was performed for some decorative ceramic glazes in the PbO–SiO<sub>2</sub>–Na<sub>2</sub>O–K<sub>2</sub>O–CaO(BaO)–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> system with addition of 10% TiO<sub>2</sub> and ZnO. The crystallization kinetics has been studied in non-isothermal conditions using DTA technique. The apparent activation energies of the crystallization processes were calculated using the Kissinger method. The main crystalline phase, which provides the decorative effect, is rutile. This has been identified by X-ray diffraction and it is clearly visible in the optical microscopy images taken in transmitted light, as needle-like or even prismatic crystals arranged in radial-fibrous aggregates.

**Keywords:** crystallized glazes, crystallization kinetics, rutile crystallization

### Introduction

The crystallized ceramic glazes used with decorative purpose consist of a vitreous matrix in which, one or more crystalline phases separate. The crystals formation takes place during the controlled cooling process of the glazes. Special decorative effects are obtained when the separate crystals have prismatic or needle-like habitus and form fibro-radial aggregates.

The presence of some ionic dyes enhances the decorative effect due to the uneven dispersal of the color between the vitreous and the crystalline phases.

Very usual crystallized glazes are those with TiO<sub>2</sub> and ZnO content [1–3] because the rutile (TiO<sub>2</sub>) and willemite (Zn<sub>2</sub>SiO<sub>4</sub>) separated as crystalline phases show a marked tendency to form prismatic or needle-like crystals (tetragonal system for rutile, respectively trigonal system for willemite).

The development of some crystals with shape and dimensions that ensure the desired decorative effects is conditioned by the use of some vitreous systems that facilitate the crystallization processes and crystals growth and also by the application of the most propitious thermal treatment conditions. Along the adequate oxide composition of the melt, the cooling rate and the thickness of the glaze layer have a determinant influence upon the crystallization processes [2].

Our experiments focused on the elaboration of crystallized glazes for faience products, having the firing temperature around 1150°C; it has been pursued the establishment of the optimal TiO<sub>2</sub> and ZnO

content, as well as a composition of the vitreous matrix to enhance the crystalline phase formation and to ensure at the same time a good accordance of the glaze and the bisque.

Within the framework of some of our previously published papers [4, 5], lead crystallized glazes have been obtained, which stand out by the fact that avoid the fritting process by using a lead silicate resulted from a precipitation reaction. The optimal composition field and the nature of the crystalline phase in these glazes have been already established in some previous papers [4, 5].

The aim of the present paper is the kinetic studies of the rutile crystallization processes from the mentioned glazes, in non-isothermal conditions. The apparent activation energies of the crystallization processes were calculated with the Kissinger method [6–10]. The rutile crystallization degree was analyzed by optical microscopy in reflected light and the nature of the crystalline phase was established by X-ray diffraction.

### Experimental

The kinetic studies of the crystallization processes have been done on glazes G.27 and G.28 [5] which were selected based on their decorative effect (resulted from the crystallization processes), reflecting at the same time essential differences concerning the proportion and the features (shape and size) of the crystalline phase.

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### Samples preparation

The recipes of the studied glazes are presented in Table 1.

The oxide composition of the two glazes is presented in Table 2.

The milling of the glazes has been done in the Pulverisette balls mill, for 5 min. The glazes have been then applied by immersion on faience plates made from the current mass used by S.C. FAIMAR S.A. Baia Mare, Romania. The firing of the glazes has been done in a laboratory kiln with SiC bars and it has been followed by cooling until the next day.

In order to perform the kinetic study of the crystallization processes, separate glaze samples have been dried, molten at 1250°C (in alumina crucibles) and then fritted (by fast cooling in cold water). After grinding in the mortar, the frits have been subjected to differential thermal analysis (DTA).

### Instrumental methods

The samples were subjected to differential thermal analysis (DTA) using a Shimadzu DTA 50 instrument. The DTA curves were recorded in air in the temperature range 25–800°C at various heating rates (2, 5, 10, 15, 20°C min<sup>-1</sup>) using a platinum cell. The sample mass was 120 mg.

The nature of the crystalline phases present in the glazes has been established by X-ray diffraction using a DRON 3 diffractometer with CuK<sub>α</sub> radiation.

The crystallization degree of the glazes and the habitus of the formed crystals have been pursued in reflected light using a Guangzhou L 2020A microscope with digital camera.

## Results and discussion

The DTA crystallization curves for the G.27 glaze at different heating rates are presented in Figs 1–3.

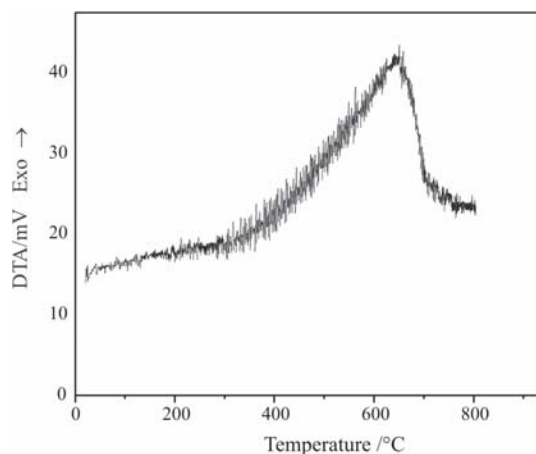
**Table 1** Recipes of the studied glazes

Glaze	Raw material/mass%								
	PbO·1.5SiO <sub>2</sub>	Feldspar	Sand	ZnO	TiO <sub>2</sub>	Pigment Zn <sub>0.5</sub> Co <sub>0.5</sub> Al <sub>2</sub> O <sub>4</sub>	Kaolin S	Wollastonite	BaO·4B <sub>2</sub> O <sub>3</sub>
G.27	55	11.5	11	5	10	1.5	1	–	5
G.28	50	11.5	11	5	10	1.5	1	5	5

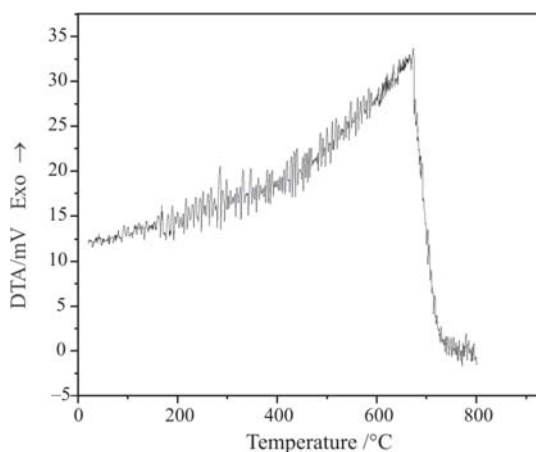
**Table 2** Oxide composition of the studied glazes

Glaze	Oxides/mol%											
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O+K <sub>2</sub> O	PbO	MgO	CaO	ZnO	B <sub>2</sub> O <sub>3</sub>	BaO	TiO <sub>2</sub>	CoO
G.27	35.25	3.08	0.030	1.15	39.19	0.060	0.19	5.34	3.23	1.77	10	0.31
G.28	36.38	3.08	0.070	1.15	35.63	0.060	2.50	5.34	3.23	1.77	10	0.31

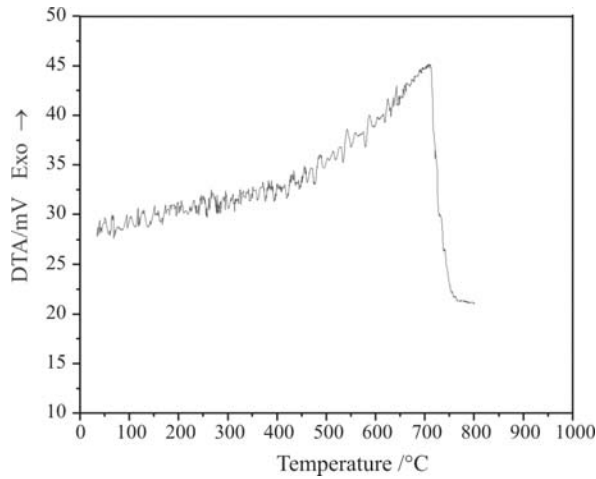
From Figs 1–3 it can be observed that the DTA curves present a significant fine structure superimposed on the main exothermic effect, more pronounced at the lower heating rates. A similar behavior was explained in the literature [11] by the uneven contact of the powdered sample with the sample pan,



**Fig. 1** DTA curve of the sample G.27 for 2°C min<sup>-1</sup> heating rate



**Fig. 2** DTA curve of the sample G.27 for 5°C min<sup>-1</sup> heating rate



**Fig. 3** DTA curve of the sample G.27 for 20°C min<sup>-1</sup> heating rate

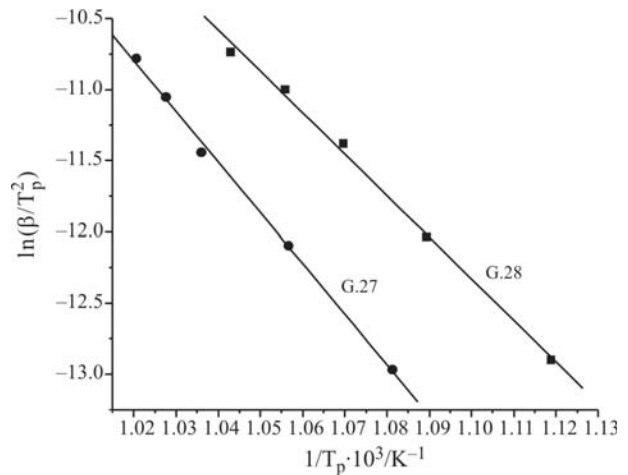
with resulting variations in the thermal contact efficiency and therefore heat transfer. Particularly, in the case of our samples the crystalline phase (rutile) represents maximum 10% from the sample, the rest being vitreous phase (in which the crystalline phase develops). This concrete situation may also influence the heat transfer efficiency.

The temperatures at the maximum crystallization rate (the temperatures of DTA peaks) for different heating rates of the samples G.27 and G.28 are presented in Table 3.

*Kissinger analysis*

Kissinger method called the maximum rate method makes possible to calculate the activation energy regardless the reaction order using the variation of the DTA peak temperature with the heating or cooling rate [6, 7]. Assuming that the temperature of the maximum DTA peak is the temperature at which the reaction rate is a maximum and the reaction order remains constant during the process, Kissinger established the equation:

$$\ln \frac{\beta}{T_p^2} = -\frac{E}{RT_p} + const. \quad (1)$$



**Fig. 4** Plots of  $\ln(\beta/T_p^2)$  vs.  $1/T_p$  for glazes G.27 and G.28

where  $\beta$  is the heating rate,  $T_p$  is the temperature of the DTA peak (the temperature at which maximum reaction rate takes place) and  $R$  is the general gas constant.

The apparent activation energies ( $E_a$ ) for the crystallization processes of the studied glazes G.27 and G.28 were calculated from the slope of the fitted linear function of  $\ln(\beta/T_p^2)$  vs.  $1/T_p$  (Eq.(1)). The plots are shown in Fig.4 and the calculated values of the apparent activation energies are presented in Table 3.

As can be seen, the apparent activation energy for G.28 glaze is slightly smaller than that of the G.27 glaze.

For a subjective assessment of the crystallization degree and the decorative effect, the digital images of the studied glazes are presented in Fig. 5.

For an objective pursuit of the crystallization degree and especially the crystals habitus, the glazes have been studied microscopically, in reflected light (Figs 6 and 7).

The shown images reveal the presence of the needle-like or even prismatic rutile (TiO<sub>2</sub>) crystals, of sizes up to 1–2 mm, disposed as feltings in Fig. 6, but also as fibrous-radial nests in Fig. 7.

It may be clearly noticed that in glaze G.28 the rutile crystals are more developed than in glaze G.27. This situation may be explained by the presence of wollastonite in G.28 recipe, respectively the presence

**Table 3** Temperatures of DTA peaks ( $T_p$ ) for different heating rates ( $\beta$ ), apparent activation energies ( $E_a$ ) and correlation coefficients ( $r^2$ ) for G.27 and G.28 samples

$\beta/^\circ\text{C min}^{-1}$	G.27			G.28		
	$T_p/^\circ\text{C}$	$E_a/\text{kJ mol}^{-1}$	$r^2$	$T_p/^\circ\text{C}$	$E_a/\text{kJ mol}^{-1}$	$r^2$
2	651.87			620.80		
5	673.41			645.02		
10	692.24	296	0.99880	661.93	242	0.99805
15	700.12			674.11		
20	706.86			685.87		

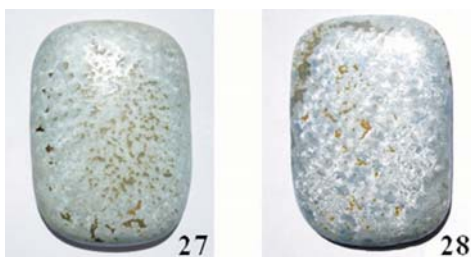


Fig. 5 Digital images of glazes G.27 and G.28

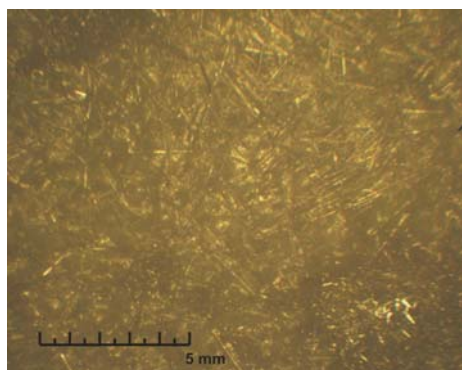


Fig. 6 Optical micrograph of G.27 crystallized decorative glaze, N=10

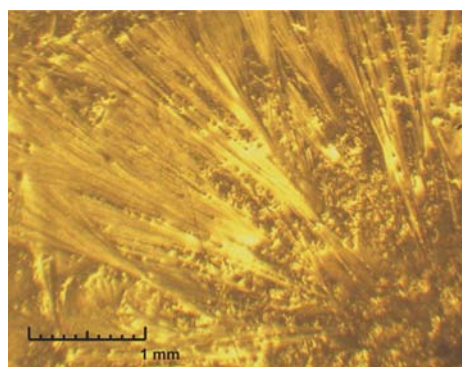


Fig. 7 Optical micrograph of G.28 crystallized decorative glaze, N=10

of CaO, which reduces the viscosity of the vitreous matrix and enhances the crystallization processes. This finding is in perfect accordance with the calculated values of the activation energies of the crystallization processes, which are smaller in the case of glaze G.28 ( $242 \text{ kJ mol}^{-1}$ ) than in the case of G.27 ( $296 \text{ kJ mol}^{-1}$ ).

The crystalline structure ascertainment has been done by X-ray diffraction analysis on the surface of the glazed samples. Figure 8 presents the X-ray diffraction pattern of the glazes G.27 and G.28, as well as the pattern of the frit obtained from G.28.

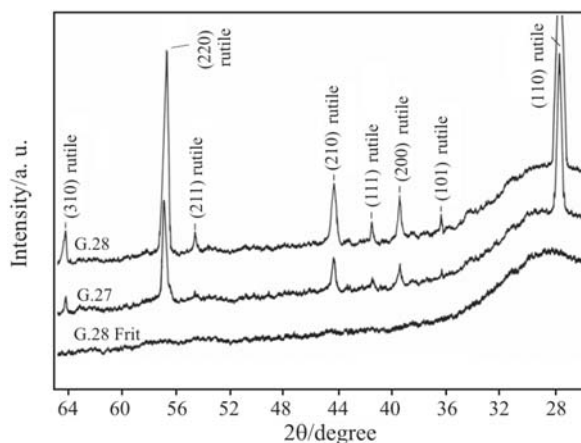


Fig. 8 X-ray diffraction patterns of glazes G.27 and G.28, respectively of the frit obtained from glaze G.28

It may be noticed that the frit obtained from G.28 is amorphous, whilst in glazes G.27 and G.28, the same crystalline phase (rutile) is present. These patterns do not show the presence of willemite, which means that ZnO is either included in the vitreous matrix or it is cryptocrystalline.

It is to be underlined that the X-ray diffraction patterns also show a higher rutile crystallization degree in the case of glaze G.28 with wollastonite – which confirms the previous observations concerning the positive effect of wollastonite upon the crystallization processes.

The presence of the crystalline phase in glaze G.28 and the lack of it in the frit obtained from the same glaze confirm the fact that the free cooling regime of the glazes in the kiln is slow enough to lead to crystallized glazes.

## Conclusions

The apparent activation energies of the crystallization processes of the studied decorative ceramic glazes present relatively high values of  $242 \text{ kJ mol}^{-1}$  for G.28 respectively  $296 \text{ kJ mol}^{-1}$  for G.27.

The apparent activation energies of the crystallization processes depend on the oxide composition of the vitreous matrix; the CaO presence in the G.28 vitreous matrix decreases the viscosity enhancing the crystalline phase development (rutile).

The smaller apparent activation energy of the rutile crystallization process in G.28 glaze is reflected in a slightly higher proportion of crystalline phase and in the habitus of the rutile prismatic crystals, with the emphasis of decorative effect.

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