

Investigation of the formation of different phases in a frittic glaze at different temperatures and pressures

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In this research, the influence of temperature and pressure on the phases formed in a defined glaze are investigated, so an initial batch including silicate, soda, calcium carbonate and boric acid with a defined seger formulation was prepared, and then it was divided into several samples. Some samples were fired at different temperatures and some of them were autoclaved at different pressures. Then the formation of different phases was investigated by X-ray diffraction. Also the microstructure of the samples was observed by scanning electron microscopy. The X-ray diffraction results showed that different phases were formed during firing and autoclaving where the firing process influenced the behavior of the solubility of the materials.

Key words: Frittic glaze, Solubility.

Introduction

The phase composition of glazes is usually controlled by the crystallization tendency of the glassy melt during cooling from the firing temperature. Crystalline phases developed in traditionally fired glazes have been found to correspond to those found in relevant phase diagrams, whereas the phases formed in shorter firing cycles depend on the reactions of the raw material [1-3].

Despite the drastic changes in firing technology during the past decades, to our knowledge, only little attention has been paid to phase formation in raw leadless glazes as a function of firing parameters [1].

The raw material composition for un-fritted matt glazes needs to be carefully selected in order to ensure the completion of the reactions during firing, and further, to achieve the desirable crystallization giving the desired surface appearance. Nevertheless, the final phase composition depends not only on the raw material and oxide compositions, but also on the firing conditions. In addition, for a given firing cycle the microstructure and durability of the surface should be taken as the key properties in selecting the glaze composition. The increased demands for wares in service, such as cleaning ability and soil repellence, have due to the latest requirements turned out to be highly-valued properties for the performance of the surface. Topographic characterization has become a common way to describe the surface properties, e.g. when estimating the soil attachment and cleaning ability of surfaces. According to our previous studies, cleaning ability was decreased by a partial corrosion of the surface,

i.e. due to the leaching of wollastonite type crystals. However, the overall cleaning ability depends on the surface roughness rather than on the phase composition [4-5].

Nucleation and crystallization of glazes and glass-ceramics are widely reported in the literature, but mostly for fritted compositions or homogeneous glasses [6-15].

When using raw glazes several different processes take place during the firing cycle, e.g. decomposition of raw materials, chemical reactions giving either crystalline or glassy products, and melting followed by nucleation and crystallization of the melt. The use of raw glazes on traditionally fired products is a well-established practice. However, the behavior of raw glazes with short firing cycles is still poorly reported in the literature [2].

One of the most important tasks of building ceramics is a selection of appropriate firing cycles as this stage of a technological process is crucial for the final properties of products. The selection of a ceramic burning temperature depends on the mineralogical composition of the raw materials, their fusion temperatures and sintering interval, the chemical composition of the raw materials, the peculiarities of the stove used for firing the samples and duration of the firing [16].

The influence of firing temperature is especially noticeable due to the formation of different phases with a high amount of additives [17].

One may find the newest publications of foreign and Lithuanian scientists, investigating interdependences among the final properties of fired samples and the maximum firing temperatures. The relationships are usually represented in a graphical form. Some authors [18-27] have investigated the interdependence of total contraction, density, water saturation and strength of different composition ceramics on the maximum firing temperature. It has been proven graphically that increasing the maximum firing temperature from 750 °C to 1050 °C results in a higher density in

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ceramic bodies, firing contraction, strength and a smaller water absorption. The Djuric *et al.* [28] have shown how ceramic density and strength change with variations in the maximum firing temperature from 1040 °C to 1080 °C. As reported [29] the change in properties (density, chemical and mineralogical composition, strength) was examined by firing the ceramics with glaze additives at temperatures from 600 °C to 1200 °C. Performing these investigations for ceramics strengths up to 90 MPa and densities up to 2560 kg/m³ have been obtained. A very topical object of ceramics investigation is the interdependence of frost resistance on the firing cycle and other technological factors. The interdependence between the maximum firing temperature (firing interval 800-1200 °C) and frost resistance and strength is described in different publications [16, 30-33]. In this study the effect of different temperatures and pressures on the phases formed with a prepared glaze was investigated.

Experimental procedures

The experimental glazes were prepared from commercial grade raw materials with a definite seger formulation (Tables 1, 2).

The glaze batch was mixed and then divided into 11 samples. 8 samples were fired at different temperatures from 200 to 900 °C with the intervals of 100 °C with a heating rate of 10 K·minute⁻¹ in an electrical furnace with

40 minutes soaking time and also 3 samples were autoclaved at different pressures (800, 1200, 1500 Pa).

The phase composition of these samples was examined by X-ray diffraction (XRD, Jeol 8030) and the morphology of the powders was characterized by scanning electron microscopy (SEM, Cambridge S360). To obtain the solubility, 3 grams of each sample were dissolved in 100 cc warm water (60 °C) and then were passed through filter. Fig. 1 shows the flowchart of the experimental procedure.

Results and Discussion

XRD analysis

Fig. 2 shows the X-ray diffraction patterns of samples

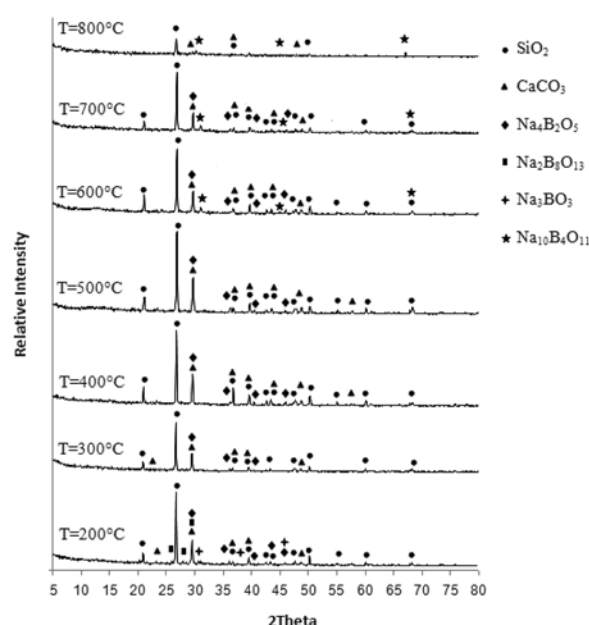


Fig. 2. X-ray diffraction patterns of the samples which were fired at different temperatures.

Table 1. Raw material composition of the experimental glaze (wt%)

Initial materials	boric acid	silica	soda	limestone
Wt%	28.85	32.54	12.70	25.90

Table 2. Oxide composition of the experimental glaze (wt%)

Oxide	Na ₂ O	CaO	SiO ₂	B ₂ O ₃
Wt%	10.46	20.10	46.15	23.29

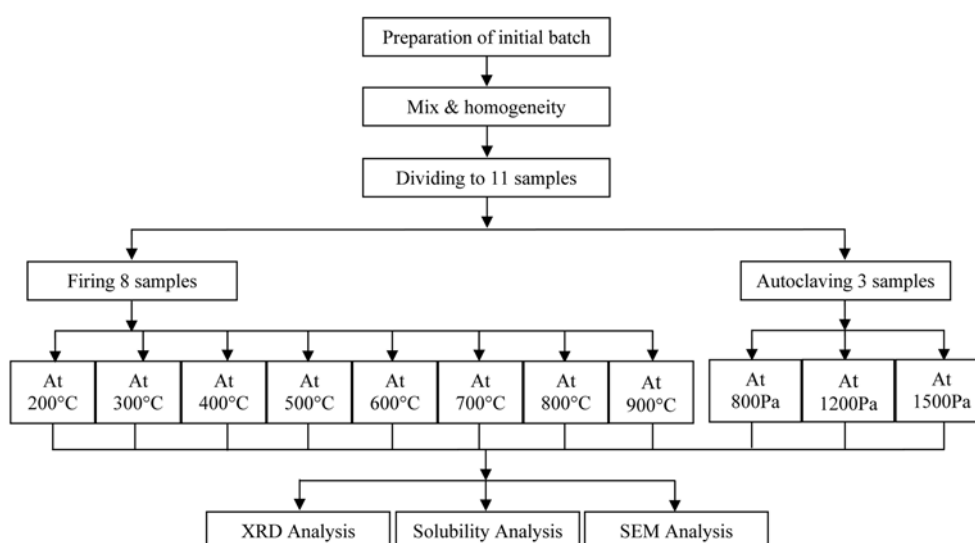


Fig. 1. Flowchart of the experimental procedure.

Table 3. The phases formed at different temperatures

Firing temperature (°C)	Phases
200	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅ , Na ₂ B ₈ O ₁₃ , Na ₃ BO ₃
300	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅
400	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅
500	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅
600	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅ , Na ₁₀ B ₄ O ₁₁
700	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅ , Na ₁₀ B ₄ O ₁₁
800	SiO ₂ , CaCO ₃ , Na ₁₀ B ₄ O ₁₁

fired at different temperatures.

All of the detected phases are listed in Table 3.

According to Fig. 2 and Table 3, SiO₂ & CaCO₃ phases exist at any temperature. As we can see the intensity of peaks of such phases decrease obviously at 800 °C. The decline in the peak intensity of CaCO₃ is due to the decomposition of CaCO₃ to CaO and also it seems for SiO₂ due to the transformation from the crystalline phase to an amorphous phase.

The Na₂B₈O₁₃, Na₃BO₃ phases were observed at 200 °C and the peaks disappeared at higher temperatures which confirm that these phases are low temperature phases. Also the Na₄B₂O₅ phase was detected at all temperatures except 800 °C. With an increase in the temperature to 800 °C it transforms to Na₁₀B₄O₁₁. According to results of the XRD analysis and solubility test the Na₁₀B₄O₁₁ is a high temperature phase and has a low solubility in water which is shown in Table 4.

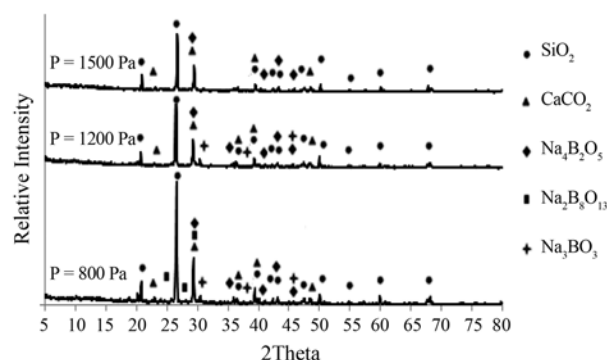
Fig. 3 shows the X-ray diffraction patterns of samples autoclaved at 800, 1200, 1500 Pa.

All of the detected phases are listed in Table 5.

According to Fig. 3 & Table 5, SiO₂, CaCO₃ & Na₄B₂O₅ phases exist at any pressure. The Na₂B₈O₁₃ phase was observed only at 800 Pa and the Na₃BO₃ phase was observed at 800 and 1200 Pa, and its peaks disappeared at a higher pressure. These results show that Na₂B₈O₁₃, Na₃BO₃ phases convert to the Na₄B₂O₅ phase with increasing pressure the same as the temperature. It is found that at a maximum

Table 4. Solubility of samples fired at different temperatures

Firing temperature (°C)	% Solubility
200	33.88
300	32.77
400	33.05
500	33.13
600	8.30
700	1.33
800	0.68
900	0.5

**Fig. 3.** X-ray diffraction patterns of the samples which were autoclaved at different pressures.**Table 5.** The phases formed at different pressures

Autoclaving pressures (Pa)	Phases
800	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅ , Na ₂ B ₈ O ₁₃ , Na ₃ BO ₃
1200	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅ , Na ₃ BO ₃
1500	SiO ₂ , CaCO ₃ , Na ₄ B ₂ O ₅

Table 6. Solubility of samples autoclaved at different pressures

Autoclaving pressures (Pa)	% Solubility
800	33.93
1200	34.00

pressure (1500 Pa) the Na₁₀B₄O₁₁ phase with a low solubility in water was not formed.

Solubility analysis

The results of the solubility test are indicated in Table 4 and 6.

As these tables indicate the solubility of the samples which were fired at different temperatures lower than 500 °C were similar and also the solubility of the samples which were heat treated at a higher temperature above 600 °C has been significantly decreased. As a result, the samples which were fired at different temperatures can affect the solubility of the phases and the phases made at higher temperatures have a low solubility.

As Table 6 shows the solubility of the samples which were autoclaved at 800, 1200, 1500 Pa were similar, thus the autoclaving treatment (increasing pressure) does not have any effects on the solubility.

Microstructure analysis

Fig. 4(a-d) shows the microstructures of the samples fired at different temperatures.

As seen from Fig. 4, the particles stick together and make agglomerates or aggregates with angular shapes. The samples which were fired at 400, 600 & 700 °C show the existence of holes & porosity in agglomerates and the existence of different phases in them. It was determined that the angular particles are the silica phase, tiny particles

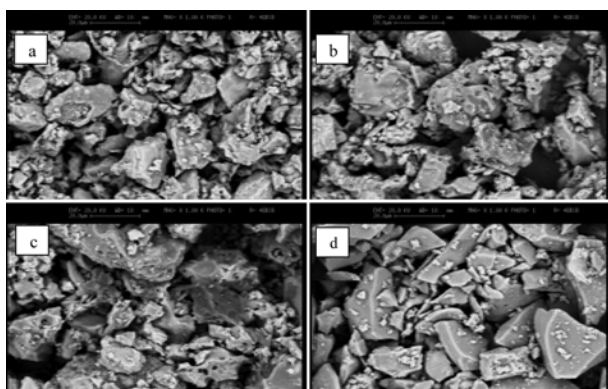


Fig. 4. SEM images of the samples which were fired at a) 400, b) 600, c) 700, d) 800 °C.

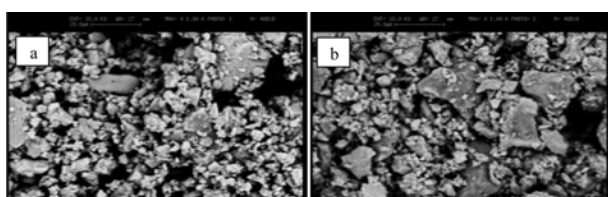


Fig. 5. SEM images of the samples which were autoclaved at a) 800, b) 1500 Pa.

are the calcite phase & spherical particles are the sodium borate phase. Also the sample which was fired at 800 °C shows that holes & porosity have been removed. It is observed that the formation of a liquid phase filled the porosity & holes after firing at a high temperature (800 °C).

Fig. 5(a, b) shows the images of samples which were autoclaved at 800, 1500 Pa respectively.

As seen from Fig. 5, the morphology of the samples which were autoclaved at 800 Pa is the same as autoclaved at 1500 Pa. These images show that with an increase in the pressure, no significant phase transformations were observed which was confirmed by XRD. Also the images show that at both pressures the morphology of particles is the same with angular shapes.

Conclusions

It is clarified that heat treatment of the samples at different temperatures has a significant effect on the formation of different phases which affect the solubility of the phases in water. Also all the crystalline phases transform to amorphous phases which is desirable for using in a glaze. The best calcination temperature of the raw materials was determined as 600-800 °C which decreased the solubility of the phases in water. Also pressure has no significant effect on the formation of low solubility phases.

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