

GLASS CERAMIC TILES FOR FLOORS BASED ON LOCAL RAW MATERIALS AND INDUSTRY WASTE

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ABSTRACT

The article presents the results of studies on the production of glass ceramic floor tiles based on local raw materials. The physicochemical properties and structural formation of glasses during crystallization were studied by X-ray analysis. According to the X-ray data, the main crystalline phase in them is anorthite-like solid solutions. Synthesized glass ceramic materials are recommended for use as floor tiles in construction.

Keywords: rocks, diabase, kaolin, glass, crystallization, anorthite, glass ceramic material.

INTRODUCTION

In construction and other industries, glass-ceramic materials, such as pyroceram, petrositals, glass crystals and others are widely used. Glass-ceramic materials obtained by a special technology, having high mechanical strength, hardness, a small coefficient of thermal expansion, and high resistance to impacts, are called glass-ceramics.

Glass-ceramics are a special class of materials that combine the properties of both glasses and ceramics. They are composed of a crystalline phase and an amorphous glass phase. This unique microstructure gives glass-ceramics a wide range of desirable properties, including: high strength and hardness, excellent optical properties, chemical resistance, thermal stability.

Glass-ceramics are made by controlled crystallization of a glass. This process involves heating the glass to a temperature where crystals can nucleate and grow. The type of crystals that form, as well as their size and distribution, can be controlled by adjusting the composition of the glass and the heat treatment parameters.

In recent years, there has been a growing interest in developing sustainable construction materials that utilize local raw materials and minimize environmental impact. Glass ceramic tiles, in particular, have emerged as a promising alternative to conventional ceramic tiles. Glass ceramic tiles are produced from a combination of glass and ceramic materials, and they offer several advantages over traditional tiles.

LITERATURE ANALYSIS AND METHODOLOGY

Since their discovery in the early 1950s, glass-ceramic materials have become widely used in: daily life (e.g. on stoves) [1], industrial applications (e.g., abrasion-resistant tiles in industrial pipes), in the environment (e.g., waste recycling) [2], biomedical applications (eg prostheses for surgical implants) [3], architectural applications [4,5] and in more advanced technological applications (eg telescope mirrors, warheads and composite materials) [6]. Glass-ceramic materials are produced from virgin glass by a sequential thermal process that includes controlled crystallization, which consists of the growth of one or more crystalline phases in a vitreous mass. Crystallization occurs in two stages: nucleation and crystal growth, which can be defined as a thermal and kinetic process in which a structurally amorphous phase (glass) is transformed into a stable solid phase with a regular ordered geometry. This ordering process is a consequence of the energy reduction that occurs when molten glass is cooled below its temperature. This phenomenon is known to the scientific community under the name "crystallization" because it is the opposite of the typical glassy nature. However, what was originally considered an



undesirable process in glass fabrication, as the origin of defects, has become an essential mechanism for obtaining glass-ceramic materials with useful processing properties.

The use of rocks and industrial waste in the production of glass-ceramic materials, the presence of Ti, Mn, Fe and other metal oxides in their composition reduces the need for their extra addition. This, in turn, leads to a reduction in the cost of production. Therefore, this study is devoted to the creation of a technology for obtaining glass-ceramic material based on less studied rocks - diabase.

RESULTS

In this work, the batch composition of glasses was selected to obtain glass-ceramic floor slabs. In Uzbekistan, such kinds are quite widespread. One of the promising objects is Arvatendiabase deposit, located in Jizzakh region, 9 km north-west of Jizzakh lime plant, 1.5 km from the village of Kuyabash. The reserves are 95 million tons. Analysis of the composition of the diabases of Arvaten deposit indicates the multi-phase nature of the studied rock. According to microscopic, X-ray and electron microscopy data, they contain 4-5 main phases in oligoclase with the formula $(Ca,Na)Al_2Si_2O_8$, orthoclase $K(AlSi_3O_8)$, iron-containing pyroxene solid solution of the augite type $(Mg, Fe^{2+})[Si_2O_6 \cdot CaFe(AlSiO_6)]$, calcite $CaCO_3$, chlorite (clinachlor) with the formula $Mg_{4.5}Al_{2.5}[OH]_8(Si_3AlO_{10})$, very little quartz SiO_2 . Minor ore minerals are also present. Crystallization of a diabase melt or a supercooled liquid also does not lead to the formation of monomineral products [7]. The results obtained indicate the multiphase nature of crystallized glasses from the rocks of Arvaten deposit after their heat treatment. In this regard, to obtain a monomineral product, they need to be batched.

The batch composition of glasses in this work was selected in order to obtain monomineral crystalline materials of anorthite composition. Diabase rocks, Angrenkaolins and alumina-containing chemical industry waste were chosen as the source of the required oxides. The chemical

composition of the experimental samples is given in Table 1. The prepared mixtures were boiled in an electric furnace with silicate heaters in corundum crucibles with a volume of 100-500 g, with a temperature rise rate of 250-300 deg/h. The glass melting temperature was 1450°C with an exposure of 1 hour. Welded glasses were poured into special steel molds in the form of sticks and discs. The glasses were not annealed to avoid the induction of crystallization. The resulting glasses were homogeneous, transparent, and had various shades of black color depending on the content of FeO, Fe₂O₃, MnO, and TiO₂ coloring oxides.

Table 1

Calculated chemical composition of the prepared batches

Content of oxides, wt. %	Indices of prepared batches							
	D1	D2	D3	D4	D5	D6	D7	D8
SiO ₂	47,98	41,05	38,63	41,07	38,65	36,24	38,67	36,25
Fe ₂ O ₃	5,85	4,55	4,5	4,31	4,26	4,21	4,02	3,97
FeO	7,70	5,87	5,87	5,49	5,49	5,49	5,1	5,1
TiO ₂	1,79	1,36	1,36	1,28	1,28	1,28	1,19	1,19
MnO	0,10	0,08	0,08	0,08	0,07	0,07	0,07	0,07
Al ₂ O ₃	13,48	26,68	29,37	27,8	30,5	33,2	31,6	34,33
CaO	8,46	6,47	6,46	6,05	6,04	6,04	5,69	5,62
MgO	5,81	4,46	4,44	4,18	4,17	4,15	3,89	3,88
K ₂ O	2,86	2,23	2,21	2,12	2,09	2,06	1,98	1,95
Na ₂ O	1,28	1,02	1,00	0,98	0,96	0,93	0,92	0,89
SO ₃	0,25	0,20	0,20	0,18	0,18	0,18	0,16	0,16
L.O.I.	4,69	6,03	5,88	6,46	6,31	6,15	6,71	6,59

The production of glass-ceramic products under industrial conditions is currently based on two basic production schemes that differ in the method of molding: according to the glass technology and the ceramic technology [8].

Known schemes for the production of glass-ceramic floor slabs according to the so-called of glass technology include the following production stages: batch preparation → melting and production of sheet glass

(1450°C) → glass cutting to specified dimensions → 1st crystallization stage (800°C) → 2nd crystallization stage (1100°C) → annealing and cooling → control and packaging → warehouse for finished products.

Industrial schemes for the production of glass-ceramic plates according to the so-called ceramic technology includes the following production stages: batch preparation → glass melting (1450°C) → granulation → grinding of glass into fine powder → preparation of a technological mixture → product molding → 1st crystallization stage (800°C) → 2nd crystallization stage (1100°C) → annealing → control and packaging → warehouse for finished products

All types of technological schemes include the stage of batch preparation. To ensure optimal conditions for melting glass, it is necessary to obtain a mixture of the required dispersion. Depending on the initial state of the raw material component, a grinding scheme is used to bring it to the required degree of dispersion. Lump diabase is subjected to coarse grinding in a jaw crusher, after which it enters for fine grinding in a hammer crusher. The selected fraction should have a particle size of no more than 1 mm. Enriched kaolin AKF-78 and granulated alumina-containing waste are also subjected to fine grinding in a hammer mill. The selected fraction should have a particle size of not more than 0.25 mm. Crushed diabase and alumina-containing waste, together with pre-dried kaolin, enter the mixer to obtain a homogeneous technological mixture. The resulting homogeneous mixture is subjected to moisture within 2% and then subjected to granulation. The granular charge is sent to the bath furnace.

The next general stage is glass melting. The glass melting temperature of the developed compositions is in the range of 1450°C. Upon completion of the processes of homogenization and clarification, the glass mass enters the production by molding or granulation.

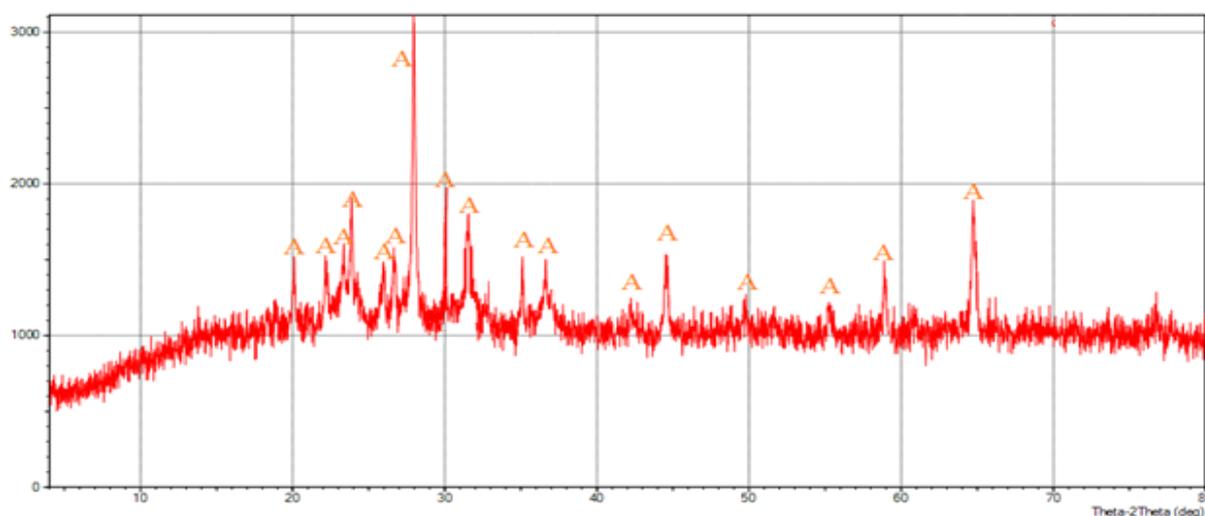
For products obtained by glass technology at the molding stage, the following is carried out: glass production, glass cutting,

end processing. Glass production is carried out at a temperature of 1250°C. The thickness and dimensions of the product are selected depending on the requirements. After processing the end parts, the semi-finished products are sent for heat treatment.

For products obtained by ceramic technology, after the completion of cooking, the following is carried out: glass granulation, granulate grinding, introduction of binders, molding. For granulation, the clarified glass melt is poured into water, where it breaks into small pieces of different sizes. Then they are finely ground, binders and plasticizing components are introduced, the batch is mixed and the semi-finished product is molded.

DISCUSSION

The heat treatment of the semi-finished product, carried out in order to crystallize the glass with the formation of a given phase, is carried out according to the developed regime. The processing mode includes 2 stages. At the 1st stage, the temperature is brought to 800°C at a rate of 200°C/hour and an exposure of 0.5 hour is given. The final temperature of the 1st stage is 1100°C and is reached at a rate of 100°C/hour with holding at the final temperature for 2 hours.



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Fig.1. X-ray patterns of glass samples of D5 compositions crystallized in a two-stage regime: 800°C-0.5 h and 1100°C-1 h.

The physical and technical properties of glass-ceramic are determined by the phase composition, depend on the size of the crystals and the content of the crystalline phase, as well as on its homogeneity and phase composition. The greatest homogeneity and signified finely dispersed crystallization, according to the visual assessment of chips of crystallized samples, were distinguished by samples with monomineralanorthite crystallization - D5. The phase compositions of these samples based on the investigated diabases, crystallized in a two-stage mode, were determined by the X-ray method (Fig. 1). Analysis of the obtained diffraction patterns revealed the presence in the samples of crystallized glasses of only one crystalline phase - anorthite (0.153, 0.162, 0.168, 0.171, 0.176, 0.180, 0.184, 0.188, 0.304, 0.318, 0.334, 0.344, 0.377, 0.403 and 0.468 nm).

Table 2

Physical and chemical properties of the obtained glass-ceramic materials

№	Density, kg/m ³	CLTE $\alpha \cdot 10^{-7} \text{K}^{-1}$	Micro hardness MPa	Abrasion, g/cm ²	Bending strength, MPa	Compressive strength, MPa	Chemical resistance, %		
							conc. HCl	35 % NaOH	conc. H ₂ SO ₄
D1	2800	55,50	8150	0,007	115	500	96,50	93,20	98,00
D2	2850	54,25	8280	0,006	122	690	96,89	94,50	98,35
D3	2900	52,08	8440	0,005	128	730	97,67	95,98	98,00
D4	3000	51,76	8580	0,005	132	750	98,20	99,00	98,50
D5	3100	48,04	8850	0,003	140	800	98,98	99,83	99,92
D7	3090	50,24	8670	0,004	135	770	98,30	99,68	98,50

It can be seen from the data in Table 2 that the samples crystallized in a two-stage regime have high physicochemical and mechanical properties, significantly exceeding those of their original glasses, which is the result of the formation of a finely dispersed crystalline structure.

CONCLUSION

The results of the experiment show that the obtained glass crystals have high physical and technical characteristics. Based on the optimal composition of D5, it is possible to produce glass-ceramic floor tiles. The resulting glass-ceramic materials are used in construction, they are also used for floor glass-ceramic slabs, external and internal wall cladding, and for other purposes.

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