
Short Communication

Foamed glass-ceramic materials based on oil shale by-products

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The feasibility and features of the production of foamed glass-ceramic materials based on oil shale ash were investigated. The optimal regime of synthesis found involved the following steps: glass fusion at 1400°C, preparation of the glass powders and blending with the foaming agent. The foaming was carried out at 900 to 920°C with a further one-stage crystallization at 790 to 820°C. It was noted that the admixture of calcium carbonate, as a foaming agent, changed the phase composition of the resulting glass-ceramics by an increased rate of the crystallization process and the intensive formation of gehlenite simultaneously with diopside.

1. Introduction

The analysis of publications related to the production of glass and glass-ceramic materials suggests the extended interest towards the use of different slag and ash wastes of metallurgy and heat power stations [1 to 5]. These wastes and by-products can be considered as quite promising raw materials for the production of glass-ceramics of the diopside type that are effective in the manufacturing of different construction materials [5 to 6]. The base system of $R_2O-MgO-CaO-Fe_2O_3-Al_2O_3-SiO_2$ is characterized by a very wide isomorphism and allows varying the chemical composition of raw materials without significant changes on the final product properties.

The chemical composition of the aforementioned oxide system is close to the composition of industrial wastes of oil shale mining and thermal treatment. It has been shown [7] that various glass and glass-ceramic materials can be produced on the base of such wastes. However the high variability of the oil shale chemical composition, even from the same deposition, leads towards research related to the manufacturing of glass-ceramic materials of not very strong requirements, such as the technologies of application for traditional glass. Foamed glass-ceramics based on oil shale are most promising materials showing good heat and noise insulation properties, having many advantages over other types of porous insulating materials, such as lower density and

water absorption, and higher heat capacity, fire resistance and chemical durability in aggressive conditions. However, for the production of insulating foamed materials special requirements must be considered, such as the optimal ratio of viscosity to surface energy in the foaming temperature interval, which favors the effective formation of gas bubbles and solidification of the foamed material. Another interesting characteristic of the oil shale ash is the low alkali concentration, which can increase the electric conductivity of the final material. The objective of this research was the investigation of the optimal conditions for the manufacture of foamed glass-ceramic materials of the pyroxene type based on oil shale ash.

2. Experimental

Oil shale ash produced by the heat power station of Syzranskaya (Russia) was used as the raw material, its chemical composition (in wt%) was the following: 41.8 SiO_2 , 12.5 Al_2O_3 , 8.5 Fe_xO_y , 21.3 CaO , 2.0 MgO , 0.7 TiO_2 , 0.8 P_2O_5 , 0.8 Na_2O , 1.6 K_2O , 7.7 SO_3 and 2.3 H_2O . Some admixtures were employed in the batches as follows: sodium salts to favor glass melting, sand and carbon to regulate the crystallization properties and Cr_2O_3 (0.7 wt%) as a nucleation agent.

Table 1 presents the batch compositions, which were melted at 1400°C during 1.5 h. The molten glass, cooled down to 1200°C, was used in the different ways for the following purposes. Preforms were produced by casting

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Table 1. Composition of batches (in wt%) and technological properties of obtained glasses

	batch no.		
	1	2	3
<u>raw material</u>			
oil shale ash	80	80	80
soda ash	—	16	—
Na ₂ SO ₄	17	—	12
sand	—	4	8
carbon	3	—	—
<u>technological property</u>			
temperature at the beginning of fusion process in °C	1180	1150	1130
Littleton temperature in °C	870	920	950
interval of bulk crystallization temperature in °C	850 to 900	750 to 820	—
interval of surface crystallization temperature in °C	800 to 850	750 to 820	750 to 850

onto a metal plate to investigate the optimal crystallization regime; fibers were drawn and used to determine the Littleton temperature by method of English (GOI viscometer, Russia), and fritted glass was produced by water quenching for the production of foamed glass-ceramics. Prior to the foaming processing, the latter was ball-milled to a specific surface area of 4500 to 4800 cm²/g (as measured by the BET method, Russian equipment LHM-8MD). The foaming agents employed were limestone, sodium meta-silicate and oil shale (48 % mineral part), added in the range of 1 to 5 wt% of the glass powder. The mixtures of glass powder and foaming agent were further ball-milled together during 30 min.

During the thermal treatment of the aforementioned mixtures, the volume variation was selected as the foaming parameter and monitored online for experiments at different temperatures. The device used for this purpose comprised a stainless steel cylinder (3 cm diameter) partially filled with the powder mixtures; an inner stainless steel plate (thickness 0.32 mm) was placed onto the powder and its other face was connected, with a nickel-chromium wire, to an electro-magnetic sensor to detect the movement of the wire as a result of the volume change. The expansion ($\Delta V/V_0$) of samples at different temperatures in the range of 700 to 1000 °C was investigated.

In accordance with previous research [7] an intensive one-stage bulk crystallization of pyroxene glass compositions took place at 790 to 820 °C. The foamed samples were treated at 800 °C for one hour and cooled to room temperature at a rate of 300 K/h.

Standard test methods of ASTM C240-97 were used to measure density, flexural strength and thermal conductivity of the obtained foamed glass-ceramic samples.

The structure and chemical composition of the glass-ceramics were investigated by scanning electron microscopy (Jeol, model 6300 (Japan)) equipped with X-ray microanalysis and also by X-ray diffraction (Philips, model X'Pert-MPD (Netherlands)). The 3-point flexural strength of foamed glass-ceramic rods, 5 mm diam-

Table 2. Comparative increase of volume $\Delta V/V_0$ (deviation $\pm 12\%$) for the mixtures of glass powder with different foaming agents (5 wt%) after the thermal treatment during 0.25 h (batch no. 2.)

temperature of thermal treatment in °C	limestone	sodium meta-silicate	oil shale
700	0.22	0.11	0.47
800	0.95	0.12	0.34
900	0.99	0.09	0.21
1000	0.74	0.06	0.07

eter and 100 mm of length, was measured from 18 specimens using the ER-5046-5 Russian equipment. The size and distribution of pores were investigated by optical microscopy (Olympus, model Vanox - AHMT-3 (Japan)).

3. Results

The technological properties of the obtained glasses are presented in table 1. The glass obtained from batch no. 1 exhibited a temperature of softening located in the interval of bulk crystallization, making it unacceptable to produce foamed glass-ceramics. The batch no. 3 was useful to obtain glass of high quality, however, bulk crystallization was not observed until 980 °C.

The batch no. 2 displayed the optimal technological properties (combination of softening temperature and crystallization properties) and required little admixtures of the cheapest components (soda ash and sand). Thus, this glass was further used to prepare the mixtures with foaming agents and produce foamed glass-ceramics.

Table 2 summarizes the results of volume increase for the mixtures of glass powder with different foaming agents (5 wt%) after thermal treatment during 0.25 h at different temperatures. The limestone admixture regis-

Table 3. Chemical oxide composition (in wt%) of glass-ceramics (batch no. 2)

crystallization method	SiO ₂	TiO ₂	Al ₂ O ₃	Fe _x O _y	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	SO ₃
casting	44.7	0.6	12.7	6.7	0.7	22.5	1.2	2.4	1.4	0.4	6.7
fritting/milling/foaming	44.5	0.6	12.5	6.6	0.7	23.8	1.2	2.1	1.2	0.4	6.4

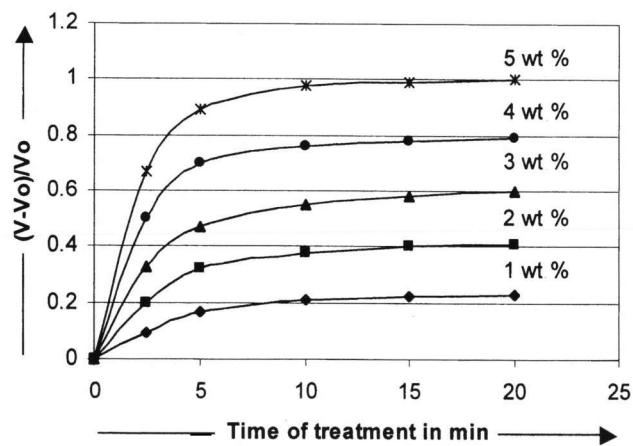


Figure 1. Kinetics of foaming for the different admixtures of limestone at 900°C.

tered the highest expansion values and was selected as the subsequent foaming agent, which was added in variable amounts in foaming experiments at 900°C. The kinetic results are presented in figure 1; higher contents of limestone promoted increased expansion and it appears that after 10 min of processing the rate of expansion was fairly small for all cases.

After thermal treatment of the glass powder mixture with 5 wt% of limestone at 900°C during 0.25 h followed by crystallization (800°C, 1 h), glass-ceramics of the chemical composition presented in table 3 were obtained. Figure 2 shows a micrograph and figures 3a and b present the diffractogram of such material. The glass-ceramic structure showed the formation of small-sized (<1 µm) crystals within the glassy matrix; the dark areas are pores present in the microstructure. The main phases observed were different pyroxenes and gehlenite and

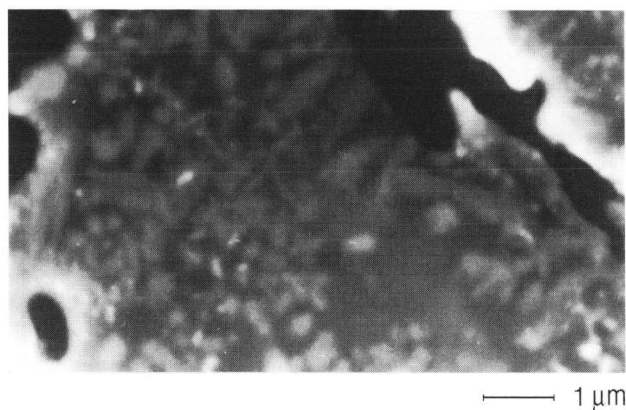
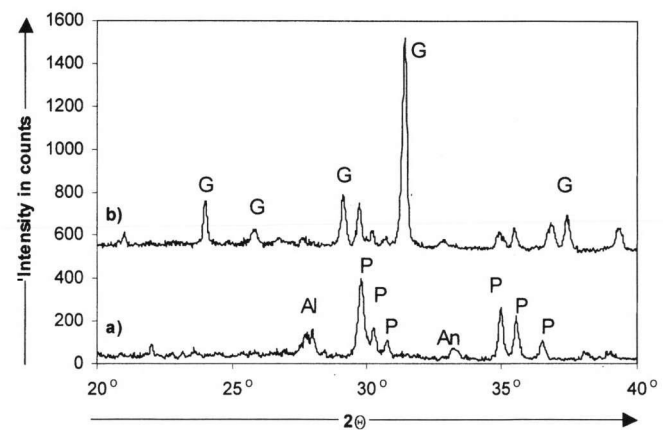


Figure 2. Scanning electron microscope photograph of foamed glass-ceramics.



Figures 3a and b. X-ray diffractograms of a) cast and b) foamed glass-ceramic samples; P = pyroxenes, An = andradite, Al = albite, G = gehlenite.

minor phases such as albite, andradite and parawollastonite.

The properties of samples obtained with the optimal regimes of treatment mentioned above were as follows: density of 350 kg/m³; porosity of (86 ± 8)% with two main types of pores, open (50 to 120 µm in diameter) and closed (5 to 20 µm in diameter); thermal conductivity of 0.10 to 0.13 W/(m K), similar to the commercialized (Russian standard GOST 24748-81) for foamed glass (0.07 to 0.10 W/(m K)); flexural strength of (3.0 ± 0.5) MPa, much higher than that of the latter standard (0.3 to 0.8 MPa).

4. Discussion

The experiments related to the application of different foaming agents showed that sodium meta-silicate and oil shale were ineffective as foaming agents since their temperatures of intensive decomposition (250 to 450°C and 450 to 700°C, respectively) were lower than the glass softening temperature (850 to 920°C). The admixtures of limestone, which can dissociate to lime and CO₂ at 700 to 950°C, rendered the best results among the foaming agents used (table 2) and are acceptable for the practical application, taking into account the registered rate of foaming as well as the overall cost. It is also noteworthy that the synthesized glasses are characterized by high concentrations of SO₃ and Fe_xO_y, which encourage the process of gas bubbles formation [8], and are especially promising to produce foamed materials.

At temperatures above 950 °C the foamed glass collapsed as a result of the fluidization of the cylinder samples. The lower foaming temperature below 750 °C was also inadequate due to the early surface crystallization that decreased the average flexural strength of samples from 3 to 1.5 MPa.

The maximal increase of volume as a result of the foaming was obtained by treatment for about 15 min at temperatures in the range of 900 to 920 °C. Limestone admixtures above 5 wt% negatively influenced the mechanical strength of the obtained samples.

It is necessary to take into account that the introduction of limestone to the glass powder influenced the phase composition and rate of crystallization. Comparison of the diffractograms (figures 3a and b) of glass-ceramics produced by casting and of those after foaming showed a change in the ratio of crystalline phases. For the conditions of casting, different pyroxenes formed the crystalline fraction, whereas the crystallization after the foaming stage showed slightly reduced intensities of the pyroxene reflections but the fraction of gehlenite was strongly enhanced.

The nature of this phenomenon is not simple and, since the chemical compositions of the cast and fritted glasses were very similar (table 3), there is possibly the influence of the additional intermediate foaming thermal treatment at 850 to 920 °C together with the relatively much higher surface area of glass powders used to produce foamed glass-ceramics, which could lead to the formation of gehlenite by surface crystallization. Comparison of the chemical composition of the pyroxenes (e.g. diopside, hedenbergite, augite) and gehlenite indicates a marked difference in the calcium/silicon ratios, which are about 0.5 and 2, respectively. The limestone addition and the foaming stage would increase the availability of calcium, promoting its chemical incorporation by means of gehlenite crystallization in the surface of glass powder particles; CaO was not detected by X-ray diffraction.

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5. Conclusion

Oil shale ash can be used in the production of foamed glass-ceramic materials. The production process included: fusion of glass based on oil shale ash with small admixtures of traditional glass raw materials (soda ash, sand); intergrinding of fritted glass with limestone admixtures (optimal of 5 wt%) up to a specific surface area of 4500 to 4800 cm²/g; foaming at 900 °C with a further one-stage crystallization at 800 °C. These technological procedures promoted good thermal insulation properties and mechanical strength of the resulting foamed glass-ceramics.

Thus, it is possible to consider the obtained material as an excellent product for thermal insulation applications in the building and construction industry.

6. References

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