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POROUS GLASS-CRYSTAL MATERIALS FOR THERMAL PROTECTION OF BUILDINGS AND STRUCTURES

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ABSTRACT

The compositions and technology of porous glass-crystal materials on the basis of siliceous natural raw materials are developed. Processes of formation of structure and properties of material are investigated. The algorithm is composed of design of material on the set of indicators.

Keywords: porous glass-crystal materials, design, mixture, research, properties, technology, production.

1. INTRODUCTION

Glass-crystal materials (GCM) are produced by stepwise cooling of the glass melts, forming a predetermined amount of the crystal phase. Features of chemical composition and microstructure provide a significant improvement of GCM properties in comparison with ceramic or glass materials.

The researches are aimed at developing effective methods of receiving GCM, produced from the widely available varieties of microporous siliceous rocks - natural gaizes and diatomites (Beregovoy, 2011; Geng, 2010; Guo, 2008).

2. MATERIALS AND METHODS OF RESEARCH

The materials were produced according to the technology, consisting of the preparatory and main stages.

The preparatory stage consisted in crushing up to 5000 … 6000 cm^2/g of pre-dried natural component - a siliceous gaize. The composition of the gaize (mass. %):
chemical: SiO_2 (87); Al_2O_3 (2); Fe_2O_3 (1,9); CaO (1,3); MgO (0,6); loss on ignition ~ (7);
mineralogical: quartz (15…20), montmorillonite (10…15), opal silicon dioxide (55…65).

The main stages of production - the obtaining of granular glass mass of a particular chemical composition and its processing in GCM. Modifying additives were the glass forming (Na_2CO_3, Na_2SO_4, Na_2SiO_3, $NaNO_3$, KNO_3, K_2CO_3) and the stabilizing substances (CaO, $CaMg(CO_3)_2$), entered into composition of raw mix in amount of 20...35%. .Before roasting, the charge material was compressed (0, 6...0, 8 MPa), and then left to stand for 1 hour at a temperature of 800...820 ºC.

Roasting of the material provided the activation process of sintering and formation of the phase composition (Beregovoy, 2008). According to x-ray phase analysis (Figure-1), it is represented by glass and a crystal phase in the form of residual quartz (Q) and its temperature modification - tridymite (T) and krystobalite (K).

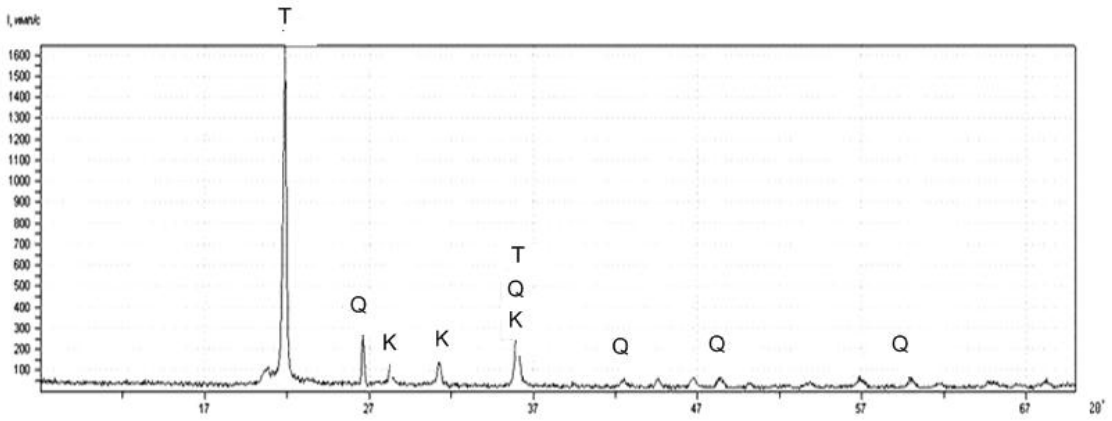

Figure-1. X-ray pattern of the gaize with an additive of Na_2CO_3 and Na_2SiO_3.

Control of structure formation processes was carried out by varying the amount and chemical composition of additives-modifiers. Raw mixes contain all oxides, necessary for formation of crystal and glass phases (SiO_2, CaO, Al_2O_3, R_2O). The source of SiO_2, CaO, Al_2O_3 and Fe_2O_3 is gaize, the source of oxides R_2O - modifiers. Figure-2 shows the scheme of the structure-forming processes, occurring during the roasting of charge material.

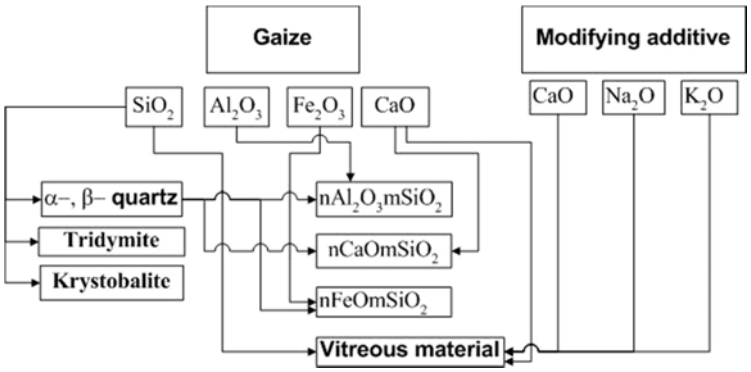

Figure-2. Scheme of glass forming processes in the charge material «gaize - modifying additive».

For determination of parameters of melting of the modified mixture the complex composition of the melt was replaced by the eutectic $CaO\text{-}Na_2O\text{-}SiO_2$ (N_2) and $CaO\text{-}K_2O\text{-}SiO_2$ (K_2) (Strelov, 1985; Maslennikova, 1991). The calculation of the minimum temperature was made by the equation

$$T_{(N_2+K_2)} = \frac{N_2 \cdot T_{N2}}{N_2 + K_2} + \frac{K_2 \cdot T_{K2}}{N_2 + K_2} \quad (1)$$

where T_{N2} and T_{K2} – respectively, the temperature of melt formation of the composition of N_2 and K_2; $N_2 + K_2$ – the total content of the melts, %.

Results of petrochemical calculations for raw mixes of the glass-crystal materials on the basis of gaize are given in Table-1.

Table-1. Amount and temperature of melt of systems (eutectic $CaO–Me_2O\text{-}SiO_2$).

Melt		Chemical composition of the raw mix, %				Temperature of the melt,°C
Type	Amount, %	SiO_2	CaO	Na_2O	K_2O	
		76,1	6,2	7,7	10,0	
N_1	36,15	73,5	5,2	21,3		725
K_1	39,84	73,0	1,9		25,1	720
$\Sigma N_1 + K_1$	76,0					723,0

At the final stage the porous GCM was synthesized from a granular glass. For this purpose granular glass was ground up in a press powder, from which was formed the raw mass and then it was foamed by roasting.

3. DISCUSSIONS

In the study of interrelationship «composition-structure-properties» were used experimental and theoretical methods of the design of composition.

The *first* method is based on statistical processing of experimental data and allows to ascertain the combined influence of 3 prescription factors (A, B, C). For example, for research the composition of porous GCM with a gas-forming additive on the basis of ground coal as varied factors have been assumed:

factor A - the content of the crushed charge material, formed by roasting at a temperature of mix 820 °C, consisting of the gaize and modifiers (% by mass of the gaize): KNO_3 (3 … 5); CaO (5 … 6); K_2CO_3 and Na_2CO_3 (18 … 20);

factor B - the content of fluxing additive ($Na_2O{\cdot}mSiO_2$ in the mix;
factor C - the content of gas-forming additive in the mix.

The process of foaming of the samples was carried out according to two modes. The mode No. 1 - slow temperature rise with a speed of 4 °C/min and maintaining at a maximum temperature (820°C) within 30 min. (Figure-3).

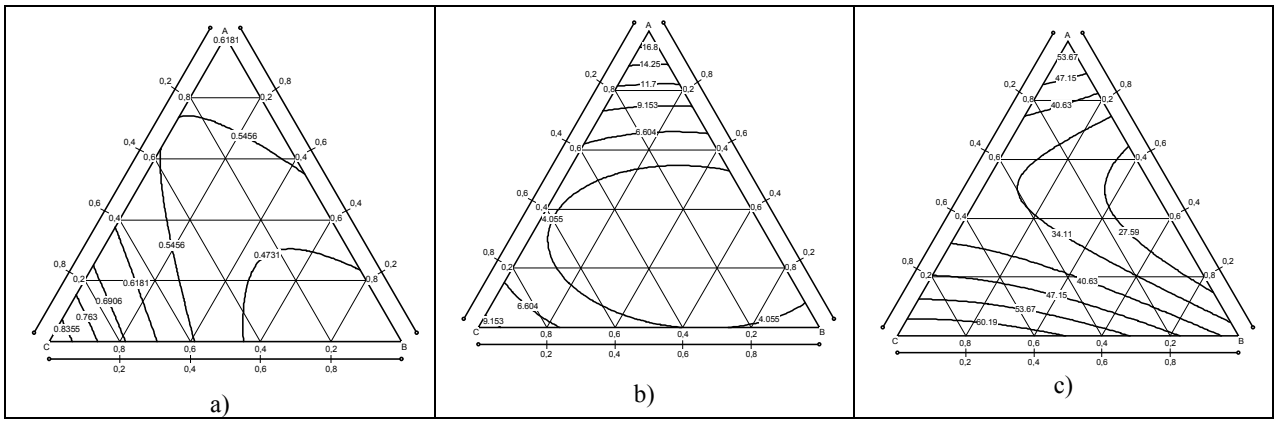

Figure-3. Influence of component composition on properties of porous GCM: a - density (g/cm^3); b - water absorption (%); c - compressive strength (kgf/cm^2)

The mode No. 2 - ultra-fast heating to a temperature of foaming (method of thermal shock). This method has allowed reducing the average density of material of similar composition at 30…35%.

The *second* design method is based on the derivation of the equations of dependence of the most important properties on parameters of the structure and their use according to the following algorithm:

a) Calculation of maximum allowable thermal conductivity of the material of matrix ($\lambda_{matrix}^{\max}$) for a given thermal conductivity of porous GCM ($\lambda_{GCM}^{req.}$)

$$\lambda_{GCM}^{req.} = \frac{\lambda_{air} \cdot \lambda_{matrix}^{\max} \cdot (1 - \sqrt[3]{V_{air}} + V_{air}) + \lambda_{matrix}^{\max\ 2} \cdot (\sqrt[3]{V_{air}} - V_{air})}{\lambda_{air} \cdot (1 - \sqrt[3]{V_{air}}) + \lambda_{matrix}^{\max} \cdot \sqrt[3]{V_{air}}}, \quad (2)$$

where λ_{air} – the thermal conductivity of air, W/(m·ºC); V_{air} - the porosity of GCM, calculated according to the equation

$$V_{air} = \left(1 - \frac{R_{GCM}^{req} \cdot m \cdot \left(\frac{W}{G}\right)^n}{0{,}7 \cdot R_{matrix}}\right)^{\frac{3}{2}} \quad (3)$$

where R_{matrix} – compressive strength of the matrix, MPa; n and m – the empirical coefficients equal respectively 3,63 and 26,3; $R_{GCM}^{req.}$ – the predetermined compressive strength of GCM, equal to maximum compressive strength of the competing analog (cellular glass 1,0 … 1,8 MPa); $\frac{W}{G}$ – mass ratio of «Water:Gaize».

b) The checking of satisfaction of conditions

$$\lambda_{matrix} \le \lambda_{matrix}^{\max}, \quad (4)$$

where λ_{matrix} – the experimentally established thermal conductivity of the base matrix composition

c) The choice of alternatives:

- the condition (4) is fulfilled, then the analyzed variant of the matrix composition is optimal and the design process is completed;

- the condition (4) isn't fulfilled, then the process of optimization of phase structure of a matrix composition using thermophysical and strength properties continues (item 4).

d) Correction of the phase composition of the GCM is made using the dependence of thermal conductivity of the matrix on the volume content of crystal and glass components:

$$\lambda_{matrix} = \frac{\lambda_{cr} \cdot \lambda_{gl} \cdot (1 - \sqrt[3]{V_{cr}} + V_{cr}) + \lambda_{gl}^2 \cdot (\sqrt[3]{V_{cr}} - V_{cr})}{\lambda_{cr} \cdot (1 - \sqrt[3]{V_{cr}}) + \lambda_{gl} \cdot \sqrt[3]{V_{cr}}} \quad (5)$$

where V_{cr} – the relative volume of a crystal phase; $\lambda_{cr.}$ and $\lambda_{gl.}$ - respectively, the thermal conductivity of crystal and glassy phases, W/(m·°C).

e) The checking of possibility to increase the heat-insulating properties of the material of matrix due to the volume content of the glass phase without changing the component composition of raw mix (changing of parameters of roasting):

$$\lambda_{gl} << \lambda_{matrix}^{\max} < \lambda_{cr} \quad (6)$$

f) Correction of the chemical composition of a glassy phase, if the condition (6) isn't fulfilled (item 7).

g) The choice of chemical modifiers taking into account the influence of their oxide composition on heat-conducting and mechanical properties of the glassy phase.

Values of the coefficients, with consideration of the additive influence of oxidic composition on strength (k_i) and heat-conducting (λ_i) indicators of glassy phase GCM, are given in Table-2 (Pavlushkin, 1973).

Table-2. Influence of oxides as a part of a glassy phase on indicators of properties.

Oxides	k_i	λ_i	Oxides	k_i	λ_i
Na_2O	0,6	0,0065	Al_2O_3	1	---
K_2O	0,05	0,0024	B_2O_3	0,9	0,0066
MgO	0,1	0,0134	P_2O_5	0,76	0,0056
CaO	0,2	0,0116	SiO_2	1,23	0,0087
PbO	0,48	0,0020	BaO	0,62	---

The analysis of experimental data and results of petrochemical calculations showed, that for optimization of the compositions using the heat-insulating indicators the following substances can be utilized:

- carbonates, sulfates, phosphates, borates and fluorides of sodium (potassium, magnesium or calcium) (Na_2CO_3, Na_2SO_4, Na_3PO_4, K_2CO_3, $Na_2B_4O_7{\cdot}10H_2O$, NaF, MgF_2 and CaF_2);
- the substances, reducing the mean free path of conductors of heat by increasing the number of the isolated tetrahedrons $[SiO_4]^4$ in the structure of the material;
- substances, promoting the scattering of energy of a heat wave due to the considerable thermal lag of the elements with the high atomic mass (PbO), which are present in their composition.

4. CONCLUSIONS

The use of the offered design methods of porous GCM allowed improving significantly the most important characteristics of the material at essential decrease of the necessary volume of experimental works.

The technology and the design methods were worked out for the compositions of porous glass-crystal materials with density of 250...1600 kg/m^3 and compressive strength of the 2....60 MPa.

Thus, it becomes possible to set purposefully the indicators of a water absorption and character of pore structure of the GCM from chemically modified natural gaize by varying the method of pore formation and the type of gas-forming additive.

Indicators of properties of the developed porous glass-crystal materials are given in Table-3

Table-3. Indicators of properties of the developed materials.

Indicators	Material of matrix	Type	
		Light weight	Particularly light weight
Density, kg/m^3	1500…1600	400…970	250…300
Strength, MPa	55…60	2,0…17,0	1,0…1,8
Water absorption, mass. %	0,15…0,20	less than 5	3,0…3,5
Thermal conductivity, W/(m·°C)	----	0,050…0,065	0,065…0,070

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