

# SHS Production of Heat-Shield Materials from Minerals and Residual Products: Influence of Preliminary Mechanochemical Treatment and Modifying Agents<sup>1</sup>

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**Abstract**—We report on preparation of porous refractory ceramics from natural quartz sand and industrial wastes (fly ash and wastes of concrete production) by SHS in a mode of thermal explosion with preliminary mechanochemical treatment of charge mixtures in the presence of carbonaceous modifying agents (activated carbon and polystyrene). The Al<sub>2</sub>O<sub>3</sub>–AlN-based composite synthesized in optimized conditions exhibited low thermal conductivity [0.185–0.228 W/(m K)], finely porous structure, and high compression strength (30–96 MPa).

**Keywords:** SHS, thermal explosion, heat-shield materials, mechanochemical treatment, quartz sand, fly ash, aerated concrete

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## INTRODUCTION

High-temperature mullite-siliceous heat insulating materials are widely used in numerous high-temperature applications such as hot-air-units of blast furnaces, calefactory and heating furnaces, etc. [1]. Refractory heat-shield mullite-based materials—3Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub>, 2Al<sub>2</sub>O<sub>3</sub> · 3SiC, 5Al<sub>2</sub>O<sub>3</sub> · 3TiB<sub>2</sub>—can also be prepared by SHS method [2–3], as well as similar aluminosilicate materials [4]. Much attention has been paid to SHS-production of corundum–silicon carbide ceramics showing high chemical inertness, abrasive resistance, mechanical strength, and heat resistance [5]. In this context, of considerable interest for SHS of high-temperature heat insulators is also the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system that yields [6] the composites containing wollastonite, anorthite, and helenite, i.e. structural elements enhancing the strength and heat resistance of synthesized materials.

As is known, oxide compounds—SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O—making the basis of most industrial wastes can also be used for SHS fabrication of structural and building materials [7, 8]. For example, the wastes of thermal power stations (incineration slag, fly ash) represent a promising raw material containing alumina–silica–calcium compounds; as well as large-volume wastes from production of aer-

ated concrete. The above wastes can be included into composition of green mixtures for use in technological combustion reactions yielding different materials, including high-temperature heat-insulators. A key role in improving the reactivity of green mixtures based prepared from technogenic wastes can be played by their preliminary mechanochemical treatment [9, 10].

In this communication, we report on preparation of porous refractory ceramics from natural quartz sand and industrial wastes by SHS in a mode of thermal explosion, with special emphasis on the influence of preliminary mechanochemical treatment and added modifying agents.

## EXPERIMENTAL

In our experiments, we used the quartz sand of the Koskuduk deposit (81.3% SiO<sub>2</sub>, 18.7% microcline K(Si<sub>3</sub>Al)O<sub>8</sub>, and 0.1–1.0% of embedded Fe, Mg, Ca, Na ions). Fly ash (from Almaty thermal power station-2) and wastes of autoclave production of aerated concrete (LLP Concrete Products, Almaty) were used as oxide components of green mixtures.

Fly ash (FA) was found to contain four components: (a) diffraction-silent matter, (b) quartz, (c) mullite [(b) and (c) in roughly equal amounts], and (d) small admixture of magnetite. Component (a)

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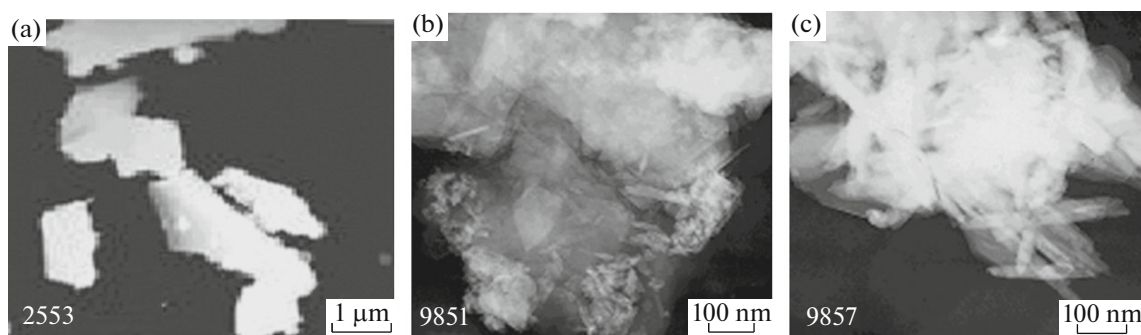


Fig. 1. ESM images of quartz particles before (a) and after MCT for 10 (b) and 20 min (c).

comprised hollow silica-based microspheres and carbon black.

The aerated concrete (AC) used in our experiments contained 34% tobermorite  $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$ , 36.6%  $\text{SiO}_2$ , 25.9%  $\text{CaCO}_3$ , and 3.5%  $\text{KAlSi}_3\text{O}_8$ . Tobermorite, or hydrous calcium silicate, is formed upon interaction of cement with water and plays a key role in the process of concrete preparation. Acicular tobermorite crystals are responsible for high strength of concrete.

Mechanochemical treatment (MCT) of powders was carried out in a Pulverizette 5 FRITZSCH ball mill (vial volume  $500 \text{ mm}^3$ , mill/ball ratio 1/4, 400 rpm, 40 g) in the absence/presence of modifying agents—activated coal (C) and polystyrene (PS). Activated coal was selected because carbon is known to act as a surfactant and reductant during intermixing of minerals (especially such as silicon and its oxides). At the same time, the MCT of quartz together with PS was previously found [11] to improve the reactivity of such mixtures in combustion reactions.

Commercial Al powder (PA4 brand) was used as a reducing agent. It was added (in amount of 37.5%) to activated mixtures of oxides (see table). Green powders (with added Al powder) were compressed (under a force of 10 tons) into cylindrical compacts 20 mm in diameter and 20–25 mm thick in the presence (5%) of added binder, natural silica gel taken from a hydro volcano in Karaganda region: 27.7%  $\text{SiO}_2$ , 14.9%  $\text{Al}_2\text{Mg}_5\text{Si}_3\text{O}_{10}(\text{OH})_8$ , 39.6%  $\text{K}_{0.7}\text{Al}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$ , and 17.6%  $\text{Na}(\text{AlSi}_3\text{O}_8)$ . The compacts were placed in a muffle furnace and held there at  $\sim 900^\circ\text{C}$  until the onset of thermal explosion (TE). Temperature profiles of TE were determined by using readings of a Raytek Ranger 3i pyrometer.

Combustion products were characterized by optical microscopy, SEM, XRD and also tested for their density, thermal conductivity, and compression strength.

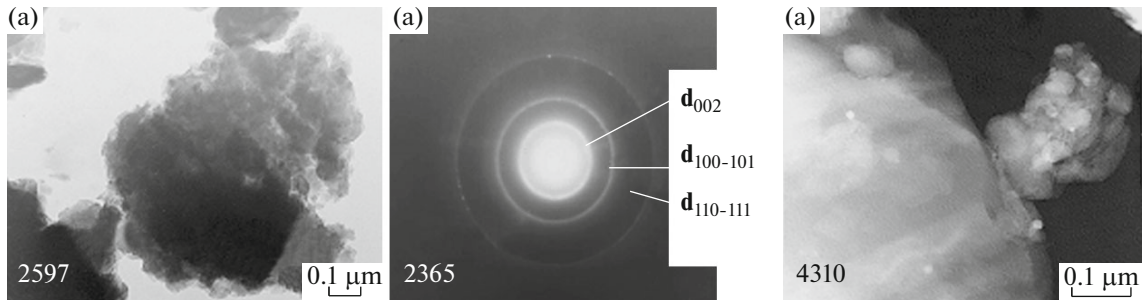
## RESULTS AND DISCUSSION

Upon milling quartz sand in a ball mill ( $\tau = 5\text{--}30 \text{ min}$ ), its bulk density  $d$  decreased from  $1.25$  to  $1.0 \text{ g/cm}^3$ . In the presence of modifying agent ( $\tau = 20 \text{ min}$ ),  $d$  attained a value of  $0.088 \text{ g/cm}^3$  in case of C and  $1.115 \text{ g/cm}^3$  in case of PS. With increasing  $\tau$  (from 3 to 30 min), the amount of milled sand particles with a size of below  $12 \mu\text{m}$  increased from 92.6 to 99.5%.

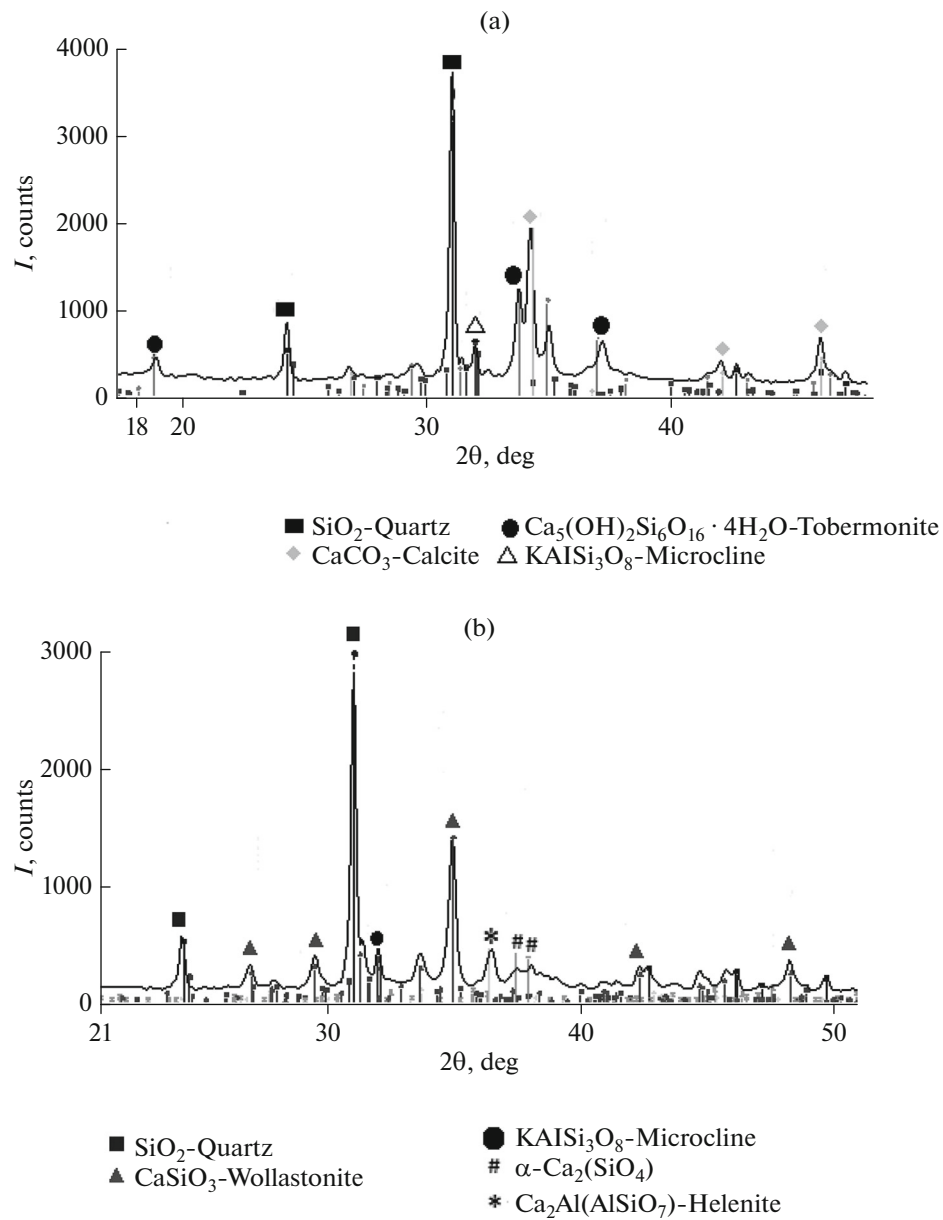
Figure 1 shows the ESM images of quartz particles before and after MCT for  $\tau = 10$  and 20 min. It is clearly seen that the MCT not only decreases the size of silica particles but also brings about deep damage on the surface of sand particles accompanied by formation of needle-like nanosized structural elements (Figs. 1b, c).

Figure 2 presents the SEM images and electron diffraction pattern of quartz particles subjected to MCT in the presence of modifying agents for 20 min. The MCT in the presence of activated coal leads to carbonization of the quartz surface (Figs. 2a) and the latter becomes loose and amorphized (Fig. 2b). In case of PS, the destruction of the quartz surface takes place in parallel with decomposition of polystyrene molecules to polyene and aromatic fragments. In this case, the active surface exhibits the presence of polycyclic aromatic molecules and polyene compounds, just as in case of soot formation during combustion of different fuels [12]. At 5% of added PS, the MCT results in the formation of a cross-linked polymer coating on the surface of quartz particle (Fig. 2c). According to [13], this can be regarded as a result of grafting the organic fragments to radical centers ( $\equiv\text{Si}^\cdot$  and  $\equiv\text{SiO}^\cdot$ ) arising on the  $\text{SiO}_2$  surface during MCT. The extent of carbonization depends on the type of modifier.

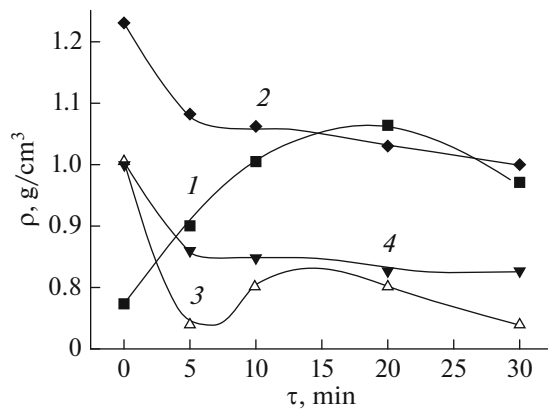
Figure 3 presents the diffraction patterns of aerated concrete before (a) and after 20 min of MCT and annealing at  $900^\circ\text{C}$  (b). Tobermorite is seen to be a predominant phase. Similar structural and morphological changes caused by MCT took place in case of fly ash. MCT results in partial decomposition of tobermorite to  $\text{SiO}_2$  and calcite. Annealing at  $900^\circ\text{C}$  leads to complete decomposition of tobermorite to wol-



**Fig. 2.** SEM images and electron diffraction pattern of quartz particles subjected to MCT in the presence of 5% C (a, b) and 5% PS (c) for 20 min.



**Fig. 3.** Diffraction patterns of aerated concrete before (a) and after 20 min of MCT and annealing at 900°C (b).



**Fig. 4.** Bulk density  $\rho$  of AC powder (1) and 50/50 quartz–AC mixture (2) containing no modifying agents and same in the presence of 5% polystyrene (3) or 5% activated carbon (4) as a function of  $\tau$ .

lastonite, helenite, and other compounds (Fig. 3b), wollastonite and quartz being the main phases.

Figure 4 shows bulk density  $\rho$  of AC powder and quartz–AC mixtures without and with modifying agents as a function of  $\tau$ . After MCT, the density of AC powder increased (Fig. 4, curve 1). Combined treatment of aerated AC–quartz mixtures also brings about some increase in the bulk density due to an increase in the packing density of powder. The use of modifying agents reduces the bulk density of powders (Fig. 4, curves 3 and 4). The presence of minimum and maximum in curve 4 (Fig. 4) can be attributed to successive occurrence of (i) tobermorite destruction, (ii) decomposition of polystyrene, and (iii) formation of new chemical bonds during the MCT. In case of carbon, the dependence on  $\tau$  is smooth.

Since some certain amount of unburnt coal is present in the fly ash, at initial stages of MCT the oxide particles are modified with its own carbon. The bulk density of FA decreases from 0.82 g/cm<sup>3</sup> down to 0.74 g/cm<sup>3</sup>

after MCT for  $\tau = 20$  min while that of 50/50 quartz–FA mixture, increases up to 0.95 g/cm<sup>3</sup>. For the materials under study, the optimal duration of MCT was found to be around 20 min [14] and this value was used in all subsequent experiments.

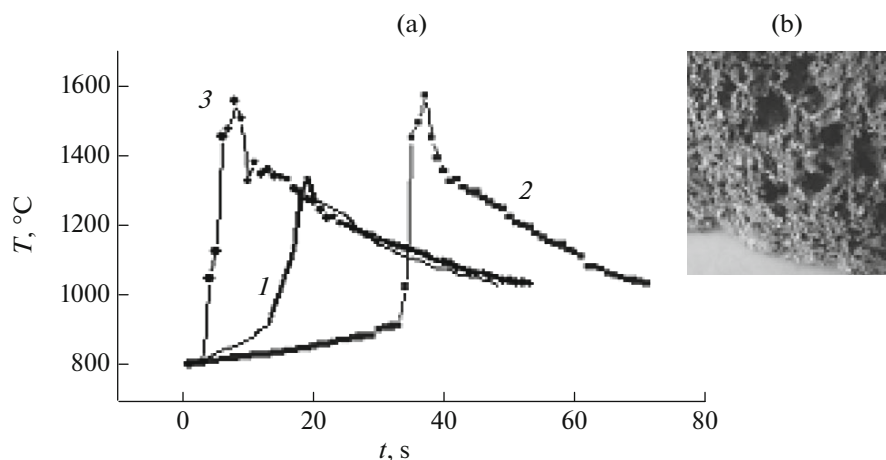
Figure 5 shows the temperature profiles of TE in the reactive systems subjected to MCT for  $\tau = 20$  min and the fracture surface of a product. It follows that the induction period for TE in case of FA (curve 2) is considerably larger; although the maximum temperature ( $T_m$ ) is higher by about 200°C. For quartz–FA mixtures (curve 3), the induction period markedly shortens, at a relatively high  $T_m$ . This is due to both an increase in the reactivity of mineral components and the activation of constituent carbon of fly ash. The activation of carbon is conditioned not only by its dispersion in a mill but also by the action electron emission arising upon mechanical destruction of quartz particles [15]. The activated carbon present in green mixtures favors the onset of TE and then takes part in the reduction of silica. Irrespective of  $\tau$ , the combustion of FA-containing mixtures (curve 2) proceeds vigorously with  $T_m$  around 1600°C and yields largely corundum and with an admixture of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Aluminum and quartz are almost completely consumed in combustion reaction. But the products derived from FA–quartz mixtures exhibit the presence of unreacted silicon and aluminum nitride. According to semi-quantitative XRD data, the phase composition of combustion products was as follows: 64.0% Al<sub>2</sub>O<sub>3</sub>, 8.2%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 18.4% Si, 1.2% SiO<sub>2</sub>, 1.2% Al, 2.7% FeAl<sub>3</sub>Si<sub>2</sub>, and 4.3% AlN.

Despite such a composition, the compression strength of the material proved to be rather low (<4 MPa), which can be explained by its loosening with evolved gases. Variation in the quartz/fly ash ratio in green composition, allowed us to increase the strength of synthesized porous materials up to 10 MPa, with a density of 1.173 g/cm<sup>3</sup>,

Compression strength  $\sigma$ , density  $\rho$ , and thermal conductivity  $\lambda$  of combustion products derived from the listed green compositions ( $\tau = 20$  min)

Charge composition	$\sigma$ , MPa	$\rho$ , g/cm <sup>3</sup>	$\lambda$ , W/(m K)
62.5% (80% SiO <sub>2</sub> + 20% FA)* + 37.5% Al	10.5	1.173	0.309
62.5% (50% SiO <sub>2</sub> + 50% FA)* + 37.5% Al	4.0	1.090	0.229
62.5% (80% SiO <sub>2</sub> + 80% FA)* + 37.5% Al	3.3	0.973	0.359
62.5% FA* + 37.5% Al	2.8	0.895	0.418
62.5% (80% SiO <sub>2</sub> + 20% AC)* + 37.5% Al	80.8	1.770	0.552
62.5% (50% SiO <sub>2</sub> + 50% AC)* + 37.5% Al	47.1	1.470	0.397
62.5% [(80% SiO <sub>2</sub> + 20% AC) + 5% C]* + 37.5% Al	23.0	1.510	0.212
62.5% [(80% SiO <sub>2</sub> + 20% AC) + 5% PS]* + 37.5% Al	96.0	1.670	0.185
62.5% [(50% SiO <sub>2</sub> + 50% AC) + 5% C]* + 37.5% Al	3.2	1.370	0.346
62.5% [(50% SiO <sub>2</sub> + 50% AC) + 5% PS]* + 37.5% Al	30.0	1.720	0.228

Asterisk indicates mechanoactivation, FA stands for fly ash, AC aerated concrete, C activated coal, and PS polystyrene.



**Fig. 5.** (a) Temperature profiles of TE in reactive systems based on quartz (1), FA (2), and 50/50 quartz-FA mixture (3) after MCT for  $\tau = 20$  min and (b) fracture surface of a product derived from mix (3).

which seems rather promising for their use as heat shields.

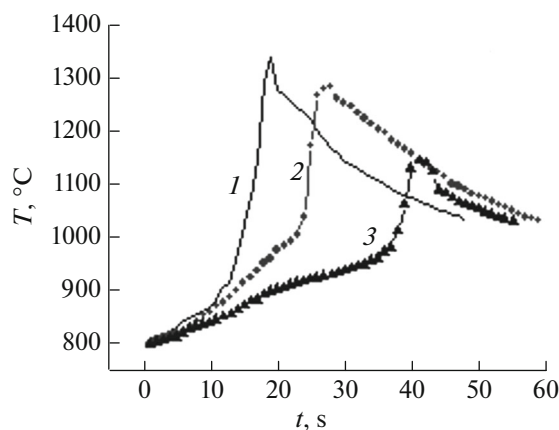
Figure 6 presents the temperature profiles of TE in reactive systems based on activated quartz-AC mixtures. In this case, the induction period for TE is seen to increase (curves 2 and 3), along with a decay in  $T_m$  caused by thermal decomposition of tobermorite. The higher AC content of green mixture, the lower burning velocity and combustion temperature. Further increase in  $\tau$  decreased  $T_m$  down to 1100°C.

Figure 7 shows the temperature profiles of TE in reactive systems based on quartz-AC mixtures activated in the absence and presence of added modifiers. Modification with C and PS is seen to markedly activate the process and increase  $T_m$ . For the system modified with carbon, the induction period of TE sharply decreases while the burning velocity and  $T_m$  grow (curves 2 and 3). In case of PS, the effect is less pro-

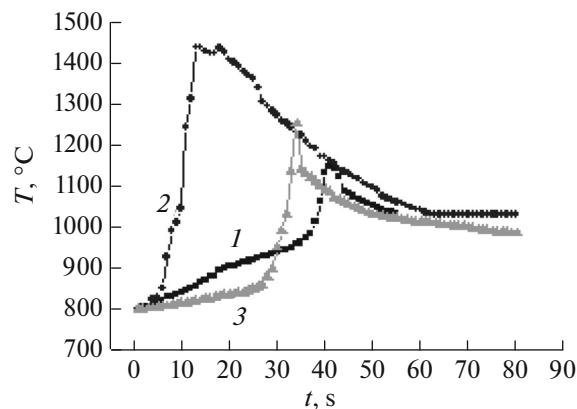
nounced. A specific feature of curve 2 is a longer dwell time at temperatures above 1050°C.

Of key importance for practical implementation is the compression strength of a given material. Figure 8 shows the compression strength of products derived from modified 50/50 quartz-AC mixtures as a function of  $\tau$ . In case of PS as a modifier (curve 1), the compression strength is seen to markedly grow with increasing  $\tau$ . In case of activated carbon, the behavior is quite opposite (curve 2). This is because the products formed in the presence of C had a loose structure (see Figs. 8b). Therefore, the materials SHS-produced in the presence of PS seem highly promising for practical implementation.

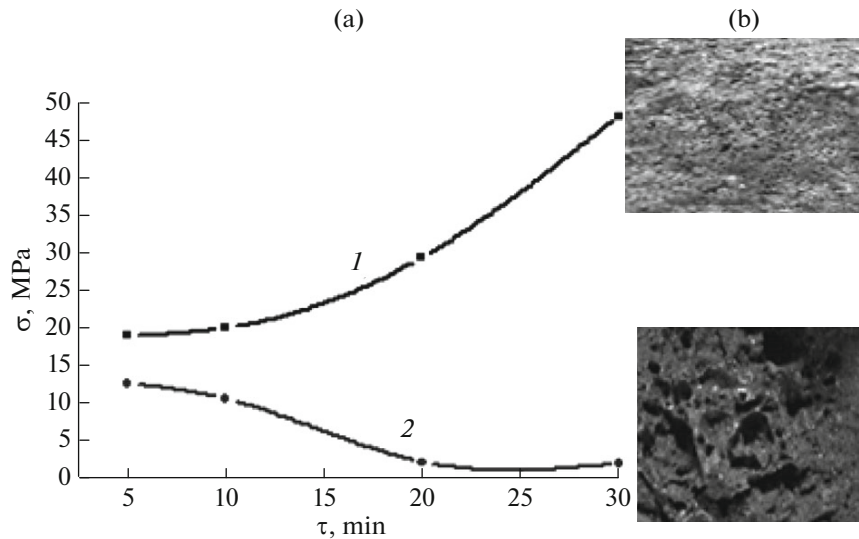
The above increase in  $\sigma$  can be associated with formation of various aluminosilicates and aluminum nitride in the course of MCT. The XRD results gave the following phase composition of materials synthe-



**Fig. 6.** (a) Temperature profiles of TE in reactive systems based on activated quartz (1) and activated 80/20 (2) and 50/50 (3) quartz-AC mixtures ( $\tau = 20$  min).



**Fig. 7.** Temperature profiles of TE in reactive systems based on activated 50/50 quartz-AC mixtures containing no modifier (1) and in the presence of activated coal (2) or polystyrene (3);  $\tau = 20$  min.



**Fig. 8.** (a) Compression strength  $\sigma$  of products derived from 50/50 quartz–AC mixtures modified with polystyrene (1) or activated coal (2) as a function of  $\tau$  and (b) respective fracture surfaces.

sized in the presence of PS ( $\tau = 20$  min): 49.1%  $\text{Al}_2\text{O}_3$ , 19.3% Si, 14.9%  $\text{SiO}_2$ , 6.1% AlN, 4.5%  $\text{FeAl}_3\text{Si}_2$ , 4.0%  $\text{NaAlSi}_3\text{O}_8$ , 0.4%  $\text{FeSi}_2$ , and 1.7%  $\text{KAlSi}_3\text{O}_8$ .

Compression strength  $\sigma$ , density  $\rho$ , and thermal conductivity  $\lambda$  of combustion products derived from activated green compositions (enlisted) are collected in table. The thermal conductivity is seen to vary within the range 0.552–0.185 W/(m·K) in line with material density (i.e. porosity).

Added PS can be assumed to play the role of stencil mask in the process of material patterning into more or less ordered structure with good compression strength. At the same time, its combustion generates a lot of gaseous products that ensure the formation of fine porous structure in final product.

## CONCLUSIONS

SHS in a mode of thermal explosion can be readily applied to fabrication—from mechanically activated natural and industrial raw materials in the presence of modifying agents—of heat-shield materials for use in calefactory and heating furnaces. Best results have been obtained with the mixtures of natural quartz sand, aerated concrete, Al powder, and polystyrene as a modifying agent. The  $\text{Al}_2\text{O}_3$ –AlN-based composite synthesized in optimized conditions exhibited low thermal conductivity [0.185–0.228 W/(m K)], fine porous structure, and high compression strength (30–96 MPa).

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