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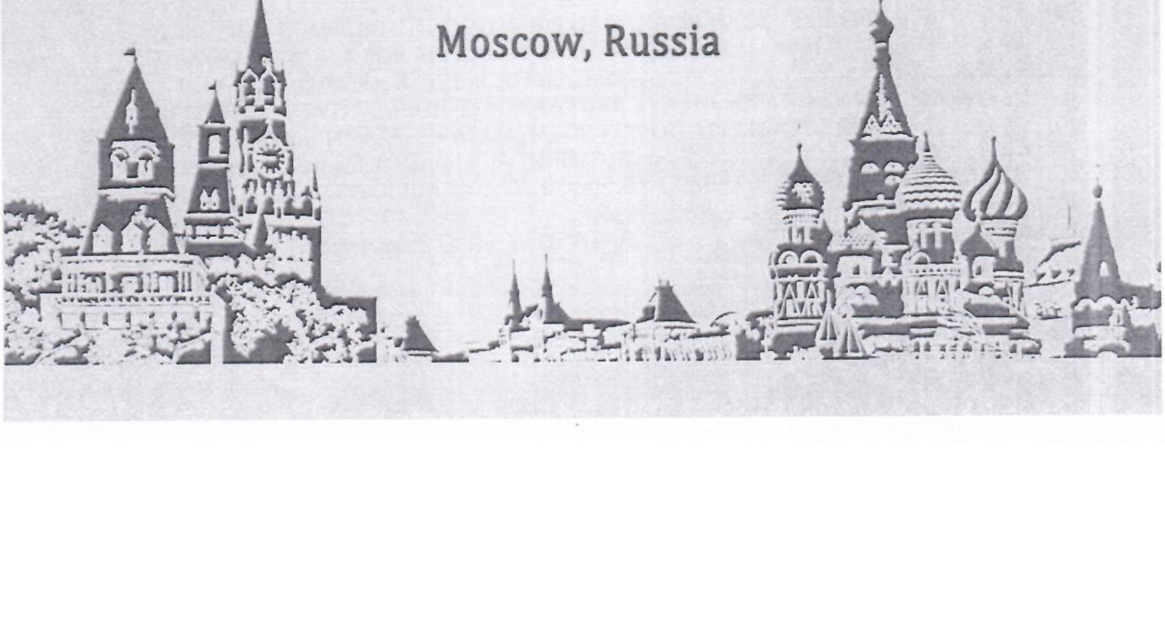

THE ROLE OF MECHANOCHEMICAL TREATMENT IN THE DEVELOPMENT OF SH-SYNTHESIS AND OBTAINING COMPOSITION SYSTEMS OF DIFFERENT PURPOSES

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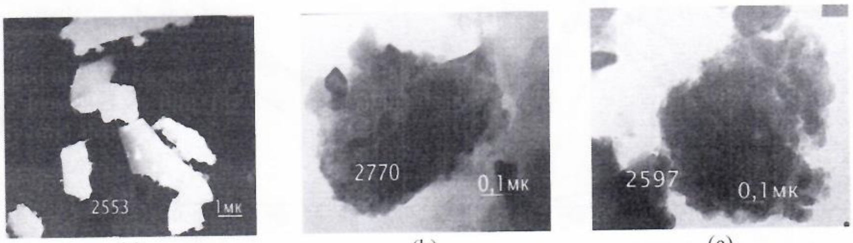
At the present, to prepare composite systems of different phase compositions with high mechanical characteristics and chemical resistance, technological combustion is widely used when, during exothermic reactions between powder components, the formation of the necessary products occurs in the mode of directional self-propagating high-temperature synthesis (SHS) [1, 2]. At the same time, much attention is paid to the process controllability and reproducibility of the final results according to the properties of the material obtained. Preliminary mechanochemical treatment (MCT) of the initial reagents used in charge mixtures for the SH-synthesis of various composites [3, 4] proved to be the most effective in terms of controlling the combustion process. Due to MCT of inorganic powder materials, not only their dispersiveness, but also the defect structure changes, mass transfer and mobility of the atomic structure get accelerated, there takes place disordering and rupture of interatomic bonds and a free-radical structure is formed. All this changes the reactivity of the materials being processed and expands the possibilities of obtaining composites in the SHS mode. By varying the pretreatment conditions, it is possible to purposefully regulate the phase and structure formation of materials during the SH-synthesis process. In this case, both individual components of the mixture, and mixtures of components are subjected to MCT. Initially, more attention was paid to the MCT of oxide systems, and then to the metal ones, which play the role of fuel in the SHS mixture [5].

In this report, several options for preparation of initial reagents (quartz and aluminum) in the MCT mode for their subsequent use as part of the SHS-charge mixture are considered. The change in the thermo-kinetic characteristics of the technological combustion and the formation of the phase composition of the synthesis products depending on the conditions of preparation of the initial reagents in the MCT were stated. We used aluminum powder of the PA-4 grade and quartz from the Kuskuduk deposit with a quartz content of 81.3 and 18.7% of microcline $K(Si_3Al)O_8$. The MCT was carried out in the presence of various organic modifying additives: carbon (graphite), butyl alcohol, polyvinyl alcohol, and stearic acid. During grinding, the amount of modifying additives introduced varied (3–20%), the grinding time was 20 min, according to the results of previous studies [4].

It is on quartz that all structural and radical transformations in the process of mechanochemical action are rather consistently studied. When an organic additive is introduced into dispersible quartz, the particle structure undergoes significant changes. The surface layer of a quartz particle is a multilayer formation with carbon structures of varying density with a thickness from 10 to 40 nm (Fig. 1). Carbonization of the quartz particle during MCT with butanol is due to destruction of the alcohol additive during processing.

The particles of the original aluminum powder are spherical in shape, with an average size of about 50 μm (Fig. 2a). After MCT of aluminum with graphite and polyvinyl alcohol, the particles have a lamellar (scaly) shape of various thickness (Figs. 2b, 2c). Aluminum particles treated in the presence of stearic acid, partially retain a spherical shape, they are encapsulated in a dense organic film (Fig. 2d) and are more dispersed than after treatment with graphite and polyvinyl alcohol.



(a) (b) (c)

Fig. 1. Electron microscopic images of quartz in the original (a) and in modified with graphite (b) and butanol (c) state.

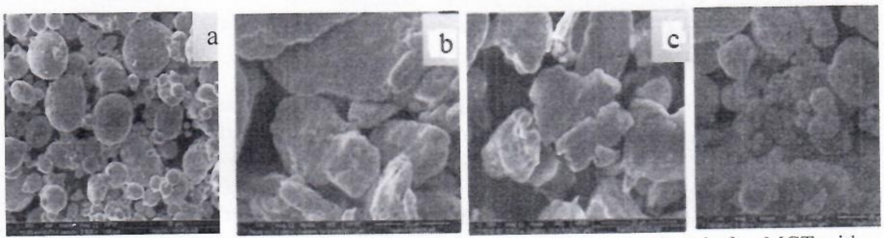


Fig. 2. Electron microscopic images of aluminum in the initial state (a) and after MCT with various modifying additives (b–d). (a) Al; (b) Al/C; (c) $Al/(C_2H_3OH)_n$; (d) Al/ $C_{17}H_{35}COOH$.

According to the results of the energy dispersive spectroscopy of the investigated aluminum powders, after MCT of aluminum with modifiers, the elemental composition of the surface layer changed. The amount of oxygen decreases, and the presence of carbon is registered, the content of which depends on the type of the modifying additive. The decrease in the content of oxygen is the result of reduction of aluminum in the surface oxide layer of the particles during the MCT process. The results of thermogravimetry, IR and EPR spectroscopy of activated and modified aluminum powder showed that during MCT there take place changes in the main spectra (new lines, frequency and strain bands are observed) and intensification of interaction processes with various components of the system. The surface of the particles is saturated with solid solutions of carbon-containing compounds. All this together should affect the activity of the processed powder. The use of such powder materials is effective, in particular, in the preparation of SHS composites with enhanced chemical and mechanical stability. So, MCT of quartz leads to the change of its maximum burning temperature with aluminum, i.e. (SiO_2 + 37.5% Al), induction ignition period, level and rate of temperature change at the post-process stage, when the phase composition of the synthesized material is actually formed (Fig. 3). Processing in a quartz mill in the presence of graphite and butyl alcohol results in a more pronounced time dependence of the maximum burning temperature.

MCT of aluminum also leads to a significant change in the thermokinetic characteristics of the combustion process (Fig. 4). The role of the modifying additive in this case is even more significant. There is a decrease in the induction period of ignition, an increase in speed and temperature at all stages of the combustion process. A distinctive feature of the combustion of such systems is a more stable, long-lasting and extensively developed combustion of the system, especially at the post-process stage.

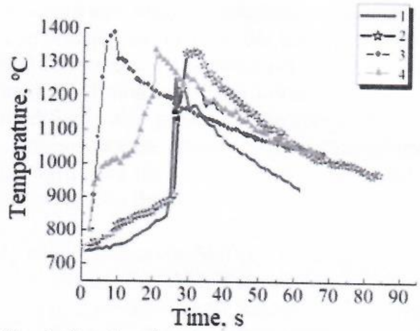


Fig. 3. Combustion thermograms for the system (SiO_2 + 37.5% Al) with non activated quartz (1) and after MCT without a modifier (2) and with graphite (3) and butyl alcohol (4) for 20 min.

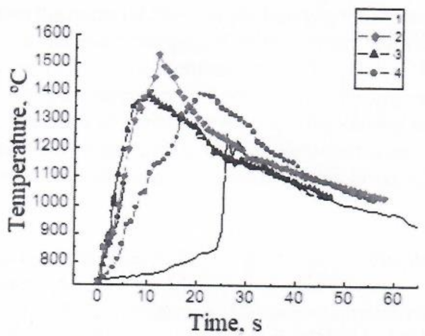


Fig. 4. Thermograms of combustion systems (SiO_2 + Al) with Al in the initial state (1) and after 20 minutes of MCT with graphite (2), polyvinyl alcohol (3) and stearin (4).

The change in the reactivity of the system as a result of MCT affects not only the thermokinetic characteristics of the combustion process, but also the composition of the final synthesis product. Table 1 presents the data on the phase composition of SH-synthesis products of the system (SiO_2 + 37.5% Al), depending on the state of the charge components after MCT of aluminum with modifying additives. Modification of the system contributes to the formation of aluminum nitride, iron and silicon disilicide, and the complex compound $FeAl_3Si_2$. The strength of the synthesized samples varies from 6.27 to 45.98 MPa. The high strength of the material is due to both the phase composition and the density of the samples. Modification of aluminum during MCT with stearic acid leads to formation of a finely porous structure due to burning out of its degradation products during MCT and in the process of SHS.

Table 1. Results of X-ray analysis of SHS samples depending on the conditions of mechanochemical treatment of aluminum with modifiers.

Phases	Phase content,%						
	Samples						
	1	2	3	4	5	6	7
Al_2O_3	43.6	67.9	77.2	65.8	61.5	65.3	51
γ-Al_2O_3				3.1	10.5		
Si	14.9	15.8	9.8	25.8	25.3	17.5	21.9
Al	10.2	2.0		1.5		5.0	11.7
SiO_2-quartz	29.9	4.1	1.2	2.8	2.7	8.0	4.2
$FeAl_3Si_2$	1.2						
AlN		1,9		1.0		1.6	6.0
$FeSi_2$		0,6	1.2			0.7	0.5
SiC- Moissanite 3C		2,1	7.8				
SiC-Moissanite 2H			2.8				
$Al_{4.59}Si_{1.41}O_{9.7}$		3,4				1.8	4.6

1 – (SiO_2 +Al), 2 – [SiO_2 + (Al + 5%C)$_{MCT}$]; 3 – [SiO_2 + (Al + 20 % C)$_{MCT}$];
4 – [SiO_2 + (Al +3% $(C_2H_3OH)_n$)$_{MCT}$]; 5 – [SiO_2 + (Al + 20% $(C_2H_3OH)_n$)$_{MCT}$];
6 – [SiO_2 + (Al + 3%$C_{17}H_{35}COOH$)$_{MCT}$]; 7 – [SiO_2 + (Al + 10 % $C_{17}H_{35}COOH$)$_{MCT}$]

Thus, from the presented data it follows that by modifying the components of the mixture, one can purposefully influence the combustion process and the formation of a dense or porous structure with ultradispersed phases that strengthen the material (the sample being synthesized). The presence of the modifier leads to a decrease in the induction period of the system ignition and an increase in the combustion rate. At the same time, in the composition of the charge, the amount of aluminum was lower than according to stoichiometry (37.5%), since the organic modifier is also present in the composites. The presence of carbon in the modifier during the synthesis process creates an inert atmosphere resulting in the interaction of aluminum with air nitrogen. The reactions of both carbide and nitrido formations are exothermic, this providing an increase in the combustion temperature.

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