The Peculiarities of Combustion and Phase Formation during SHS of Mechanically Activated Mixtures Quartz – Calcite

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Abstract

The work with the influence of mechanochemical treatment (MCT) of minerals (quartz-SiO_2, calcite-$CaCO_3$) on the process of their combustion under the conditions of SHS with aluminium. It is shown that activation of the charge mixture in the mill increases the power state of the material and contributes to the change of kinetic characteristics of combustion process: the decrease in the induction period of ignition and the increase in combustion rate. The change in combustion temperature is of a complex character due to activation of both exothermal reactions related to formation of such compounds as anothite, helenite, wollastonite. The use of deferent organic modifiers of the charge mixture results in formation of nitride and carbide compounds in the process of SHS. It is shown that changing the conditions of MCT, modifiers and ratios between the charge components it is possible on the basis of activated and modified systems to synthesize composition SHS-materials different in their phase compositions.

Introduction

SH-synthesis (technological combustion) is a unique technological process of creating composition materials for different purposes, in particular, refractories and thermal insulators. The properties of SHS-composites are determined by their phase compositions and structural peculiarities which are formed according to the regularities and kinetic parameters of combustion of multicomponent systems. Varying the initial composition and state of reagents (components) one can regulate the combustion process and form a new material the properties of which are quantitatively and qualitatively determined by synthesis products. A preliminary mechanochemical treatment (activation and modification) of the charge material components is an effective method of action on the process of their further technological combustion [1].

The use of preactivated raw material for technological combustion has been paid much attention to lately. In the process of mechanical activation solids undergo deformation and structural changes. In the course of deformation and destruction of solids there occur different powerful intermediate states. This facilitates the procedure of chemical reactions in solid phase materials, this being of great importance in technological combustion when the heat of the reaction it self is used and power supply is not required [2]. When studying the regularities of technological combustion, great attention is paid to the kinetic characteristics of the process, namely, the combustion rate (propagation of the flame front). The use of preliminary mechanical treatment of the system allows to change this characteristic of synthesis process significantly [3].

The system quartz-calcite is one of the universal ones for production of inorganic materials for a wide range of purposes developing, first of all, an increased thermal, chemical and mechanical stability. Activation and modification of the surface of the charge mixture particles provide the change of kinetic parameters of technological combustion directed to formation of structural components of SHS-composites and, consequently, their properties.

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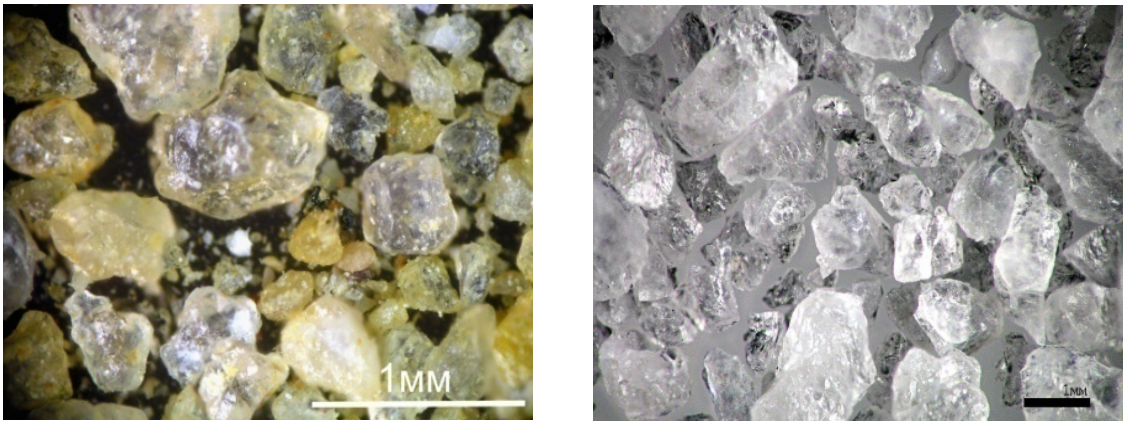
Experimental

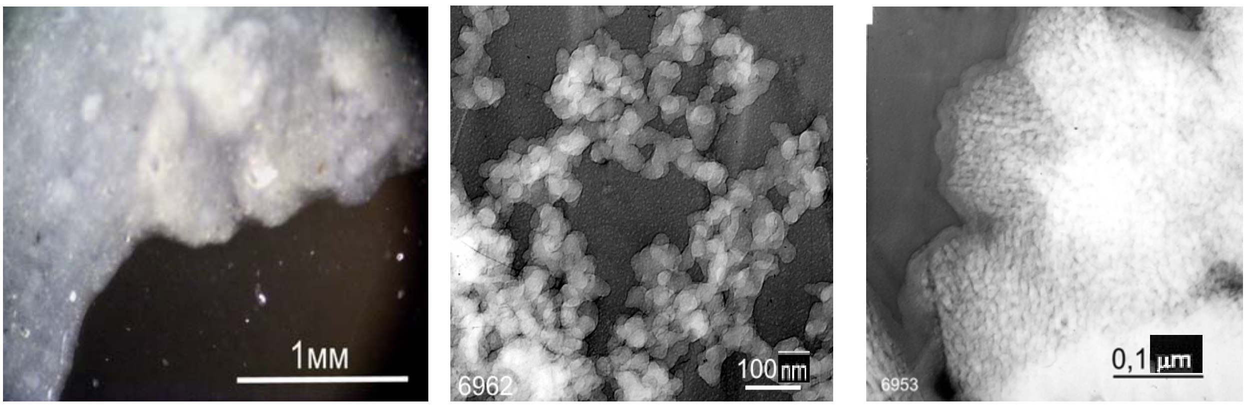
Investigations of SH-synthesis of ceramics on the basis of the system quartz-calcite-aluminium and the effect of preliminary mechanical activation on the development of SHS process were carried out in this work. Quartz and calcite were mechanochemically treated depending on time and ratio of the mass of powder to the mass of balls (M_p/M_b) and with the use of different carbon- and nitrogen containing modifiers. The experiments were carried out with both the use of synthetic analytically pure compounds and the use of natural mineral compounds. The main raw material was quartz sand of Kuskuduk deposit Fig. 1a) with the content of quarts 81.3%, besides, it contains up to 18.7% of microcline $K(Si_3Al)O_8$ as well as different elements saturating the surface and dissolved in the volume of particle. According to the results of spectral analysis, it contains from 0.1 to 1.0% of iron, magnesium, calcium, sodium which can act as active centres in the process of mechanochemical modification of the surface. The second basic component was calcium carbonate (Fig. 1b), namely, marble with the content of $CaCO_3$ – 95.7% and quartz – 4.3%. polyvinyl alcohol $(C_2H_3OH)_n$, carbamide $CO(NH_2)_2$ (in other words, diamide of carbonic acid), succinic acid ($C_4H_4O_6$) and water containing silicic acid – $H_2SiO_3{\cdot}n(H_2O)$ served as carbon- and nitrogen containing modifying additives.



a b

Fig. 1. Appearance of crystals: a – quartz sand (QS) and b – calcium carbonate

Natural silicagel from the hydrovulcano of Karaganda oblast served as a binding material. Natural gel is a whitish gelatinous mass (Fig. 2a). Being dried under the laboratory conditions by the method of suspensions, the sample consists of aggregates of compacted (20-30 nm) particles sometimes forming layer conglomerates (Fig. 2b).



a b c

Fig. 2. Morphological peculiarities of natural silicagel

According to the results of X-ray phase analysis the phase composition of natural silicagel is represented by the compounds: quartz – 27.7%, kclinochlorine 2M – $Al_2Mg_5Si_3O_{10}(OH)_8$ – 14.9%, illite 1M – $K_{0.7}Al_{12}(Si, Al)_4O_{10}(OH)_2$ – 39.6%, albite $Na(AlSi_3O_8)$ – 17.6%.

Mechanical activation of quartz sand and calcite was performed in a centrifugal-planetary mill working by the principle of gravitational grinding due to interaction of two centrifugal forces. The platform rotation velocity makes up 700 r/m and that of milling vessels makes up 1200 r/m. The acceleration value in a centrifugal-planetary mill reaches 20 g. The time of treatment varied from 10 to 40 minutes with the ratio of the mass of powder to the mass of milling balls being equal to M_p/M_b = 1/2, 1/3, 1/4. The reducing agent was aluminium APP in a stoichiometric ratio in regard both to quartz and calcite. After MCT activated powders were compacted in cylindrical samples with the diameter 20 mm and height of 20-25 mm. The samples were mould on a laboratory press "Carver" with the force 8 t. The further technological combustion was carried out in a muffle furnace at 900^0C. The temperature of combustion was measured by a pyrometric thermometer "Raytek Raynger 3i". The temperature of the sample was measured in the course of the whole SHS process.

Results and discussion

Fig. 3 presents temperature profiles of the systems containing SiO_2:$CaCO_3$ and 50:50 compared to pure quartz, the systematic investigations on the use of which in SHS were carried out earlier [1, 4]. The presence of calcite in a charge mixture results in the increase of the induction period of the system ignition and the decrease of combustion velocity. The increase in the content of calcite in the system leads to the decrease of maximum combustion temperature and the temperature of combustion at the stage of postprocesses. The temperature profiles of combustion of the systems containing quartz and calcite indicate the fact that both at the stage of mixture ignition and the stage of the combustion process completion (after the temperature maximum) there take place a great number of processes of phase formation of both endothermal and exothermal character.

After preliminary MCT the induction period reduces and the longer the treatment of mixture, the quicker the sample ignites, but the temperature of combustion considerably decreases in the course of the whole process of synthesis (Fig. 4).

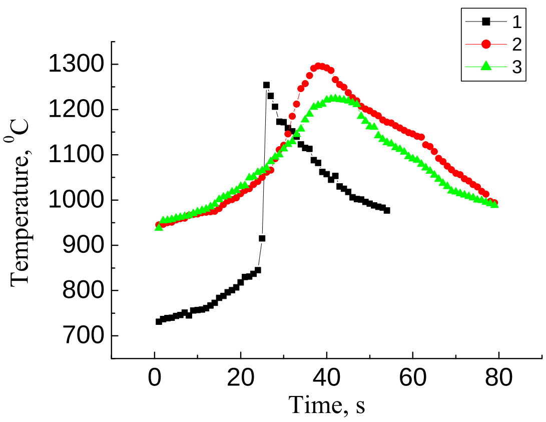


Fig.3. Thermograms of combustion for nonactivated systems: 1 - quartz with aluminium and the mixture of quartz with calcite at the ratio of the components 2 - 70:30 % and 3 - 50:50.

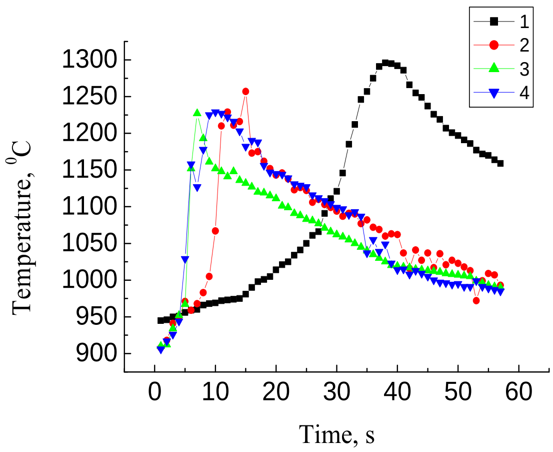


Fig. 4. Thermograms of combustion of quartz – calcite mixture with the ratio of components 70:30; 1 - a nonactivated mixture and after MCT at M_p/M_b = 1/2 during 2 - 10, 3 - 20 and 4 - 30 minutes.

A complex course of temperature curves of combustion, namely jumps in the change of temperature at different stages of the process, indicates the multistageness of phase formation both at the peak of the process and during the period of temperature decrease at the stage of postprocesses. Variations in the charge of M_p/M_b allow to exert a significant effect on the development of combustion. These dependences are especially vividly revealed after a 30 minute MCT (Fig. 5).

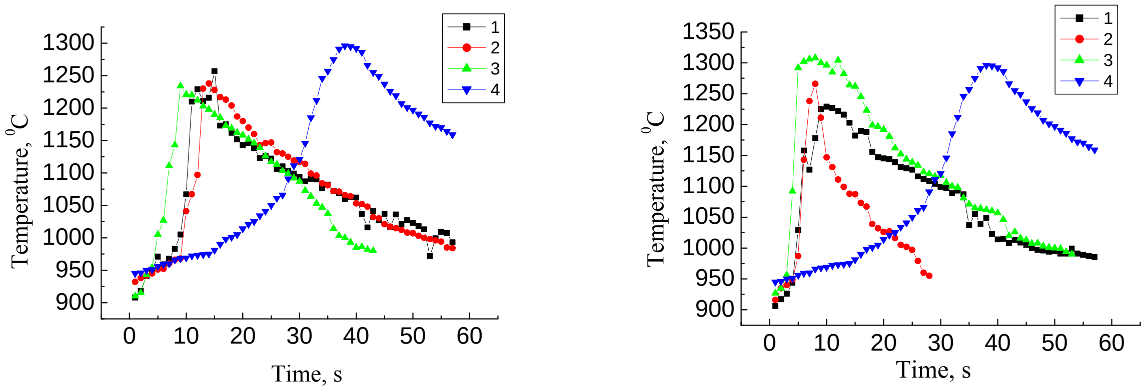


Fig. 5. Thermograms of combustion of quartz-calcite system with the ratio of the components 70/30: 1 - nonactivated mixture and after MCT at different M_p/M_b; 2 - 1/2; 3 - 1/3; and 4 - 1/4.

Integrated results on the change of maximum temperature of combustion depending on conditions of MCT are presented in Fig. 6 from which it fallows that at M_p/M_b = 1/2 the longer the period of treatment, the lower is the temperature of combustion; at M_p/M_b = 1/3 the time of treatment promotes to the increase of combustion temperature and at 20 minutes of treatment. This fact indirectly indicates deep structural rearrangements in the ground material providing the change of its thermodynamic and kinetic characteristics in the process of combustion.

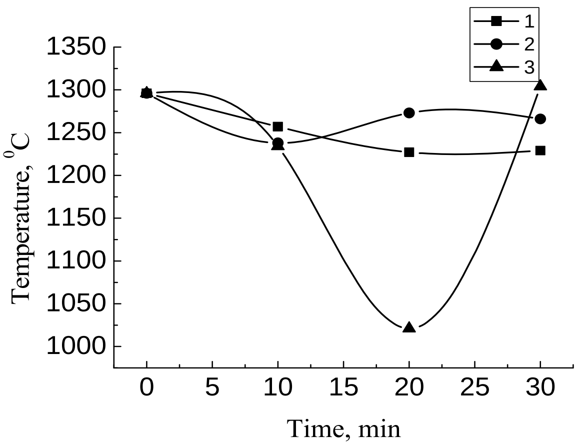


Fig. 6. The dependence of maximum combustion temperature of the system Al + (SiO_2+$CaCO_3$) on the activation time of the mixture at different ratios of M_p/M_b: 1 - 1/2; 2 - 1/3; 3 - 1/4.

According to the results of experiments on activation of combustion process of quartz with aluminium, when introducing different additives into the charge mixture, the most effective ones were silicic acid, polyvinyl alcohol and carbomide as for as activation of the combustion process is concerned: the reduction of the induction period, the increase of combustion rate and temperature [5]. A number of specific peculiarities of combustion were stated, when using succinic acid. The same additives-activators were introduced into the charge mixture of quartz with calcite at first before MCT in order to clear out the direct role of the additives themselves in the development of combustion of a nonactivated system. The results of experiments have shown that the presence of additives of polyvinyl alcohol and silicic acid in a nonactivated charge results in the decrease of combustion rate and temperature (Fig. 7). The more is the amount of calcite in the charge, the stronger is this effect. The increase in the amount of bound water in the additive contributes to the decrease of combustion temperature. On the country, the presence of 10% succinic acid in the charge results in the rise of combustion temperature of the system under study.

When introducing additives containing an ammonium group (for example, carbamide), pronounced changes are observed in the peculiarities of combustion (Fig. 7). First of all, the period of heating and ignition of the system is clearly represented by two stages: 1 – the one with low rate of temperature rise up to 1100°C during 60-80 seconds and 2 – the stage with a temperature jump almost to 1400°C during 4-6 seconds. These stages of the combustion process, in this case, are related to decomposition of not only calcium carbonate but also organic additives. Carbamide decomposes to biureate, ammonium and carbon dioxide and in the process of water vapors there can take place complete hydrolysis with formation of NH_3 and CO_2. Then oxidation of ammonia takes place, this increasing temperature and accelerating solid phase reactions in the system.

According to the results presented in Fig. 5, of the number of used additives-activators for the system (SiO_2+$CaCO_3$) the greatest thermal effect in the process of combustion was obtained in the presence of carbide and succinic acid. The presence of succinic acid provides the greatest reduction of the induction period of ignition. The next stage of the work was carried out on investigation of the combustion regularities of the system quartz-calcite activated in the presence of succinic acid depending on the time of MCT and the ratio of the mass of powder and balls.

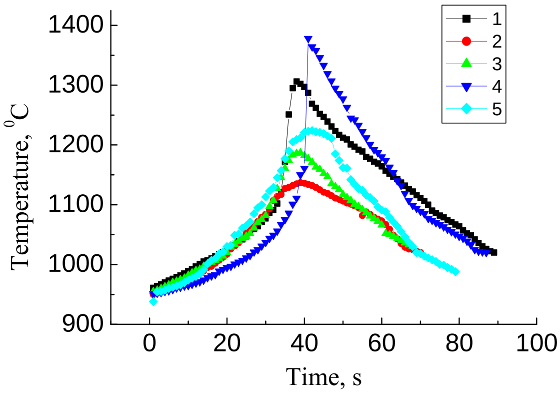


Fig. 7. Thermograms of quartz-calcite system combustion with the ratio of components 50:50 with 10% additives-activators: 1 - succinic acid, 2 - polyvinyl alcohol, 3 - aqueous silicic acid, 4 - carbamide, 5 - without additives.

The force factor of mechanical action is demonstrated through the ratio M_p/M_b: the more balls there are, the more is the number of impacts on the particle of the powder being milled the result of which is In increase in the activation degree of the material and, as a consequence, first of all the induction period of ignition reduces, the rate increases and, as a rule, the combustion temperature rises (figures).

The dependency of maximum combustion temperature on the time of MCT is of a quite complex character (Fig. 9) whit the pointof minimun volues after 30 minutes of treatment. When using other modifying additives, general regularities in the change of maximum combustion temperature depending on the conditions of MCT retain: the induction period and the level of combustion temperature change.

The main results of SH-syntesis of the systems under study are first of all determined by formation of the phase composition of the materal being synthesized on which its exploitation properties and qualite as a whole depend. For a nonactivated system containing, besides quartz, calcite in a stoichiometric ratio aluminium, in the combustion products helenite – $Ca_2Al(AlSi)O_7$ is detected in addition to corundu and silicon (Table 1).

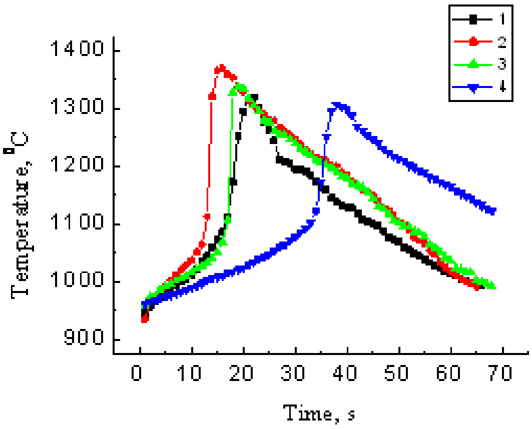


Fig. 8. Thermograms of the combustion of the system [SiO_2+$CaCO_3$+$C_4H_6O_4$] activated during 40 minutes at different ratios of M_p/M_b: 1-1/2, 2-1/3, 3- 1/4 and 4- a nonactivated system.

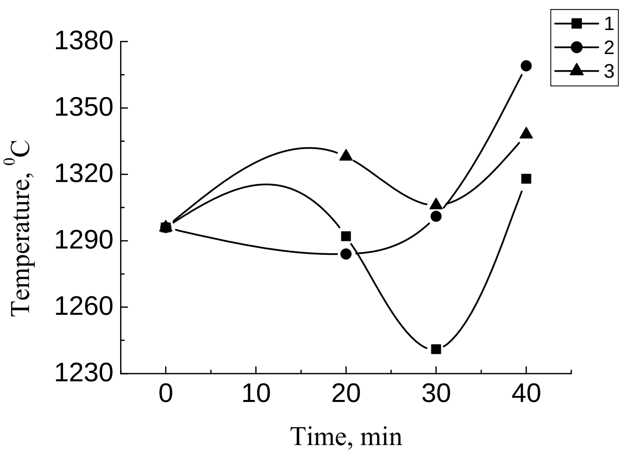


Fig. 9. The dependency of maximum combustion temperature of the system [SiO_2+$CaCO_3$+$C_4H_6O_4$] on the conditions of the combined MCT of the charge components (the time of treatment and m_p/m_b: 1 - 1/2, 2 - 1/3, 3 - 1/4).

Quite a great amount of unreacted aluminium, quartz and calcium oxide remains. After activation of minerals in the reaction products there appear anorthite $Ca(Al_2Si_2O_8)$ as well as comopunds $CaAl_4O_7$ and $Ca_3(Si_3O_9)$ the amount of which is determined by the conditins of MCT (Table 1) of great importance is the ratio of qyartz to calcite (70/30 or 50/50) in the charge.

Table 1

The phase composition of $CaCO_3$+SiO_2+Al combustion products depending on the conditions of MCT (the time of MCT and m_p/m_b)

Phases	The content of phases, %							
	Samples							
	1	2	3	4	5	6	7	8
Al_2O_3	42,7	46,6	38,3	35,3	26,3	20,8	41,2	40,6
$Ca(Al_2Si_2O_8)$			15,3	22,6	15,4	26,1		
$FeAl_3Si_2$		2,6	11,7	7,8	6,7	5,7		
Si	20,3	16,0	12,9	13,3	15,7	10,3	8,6	9,6
$Ca_2Al((AlSi)O_7$	10,5	6,8	9,7	8,2	11,4	8,8	14,9	18,9
Al	7,8	7,7	6,8	9,2	5,2	11,1	7,9	7,1
SiO_2	9,2	3,1	3,9	1,8		3,4	3,2	1,7
CaO	5,8	11,7	1,3	1,7	1,1		7,0	2,6
$CaAl_4O_7$					18,1	13,7		
$Ca(OH)_2$							2,9	7,9
$Ca_3(Si_3O_9)$							14,0	11,4
$Ca_{12}Al_{14}O_{33}$		5,4						

1 - ($CaCO_3$+SiO_2)+Al , 30/70; 2 - ($CaCO_3$+SiO_2)+Al; 50/50 3-($CaCO_3$+SiO_2)+Al, 30/70, t=10 min, M_p/M_b=1/2; 4-($CaCO_3$+SiO_2)+Al, 30/70, t=30 min, M_p/M_b=1/3,; 5-($CaCO_3$+SiO_2)+Al, 30/70, t=30 min, M_p/M_b=1/4; 6-($CaCO_3$+SiO_2)+Al, 30/70, t=20, min, M_p/M_b=1/4,; 7-($CaCO_3$+SiO_2)+Al, 50/50, t=20 min, M_p/M_b=1/2; 8-($CaCO_3$+SiO_2)+Al, 50/50, t=30 min, M_p/M_b=1/2

Introduction of different organic additives into the nonactivated charge increases the process, rate and temperature. As a conseguence, in the synthesized material of wollastonite (Table 2) were formed the amount is determined by the ratio of quartz and calcite content as well as the kind of additive-activator.

Table 2

The phase composition of $CaCO_3$+SiO_2+Al combustion products depending on the kind of additive-activators conditions of MCT (the time of MCT and m_p/m_b)

	The content of phases, %			
	Samples			
	1	2	3	4
Al_2O_3	13,2	25,8	29,2	30,4
$Ca(Al_2Si_2O_8)$			12,1	18,4
$FeAl_3Si_2$			3,4	5,3
Si	8,1	13,2	11,3	10,5
$Ca_2Al((AlSi)O_7$	5,6	11,5	17,3	14,4
Al	4,3	5,7	10.2	9,6
SiO_2	2,4		3,8	4,5
CaO	0,8	2,0	1,9	1,0
$Ca(OH)_2$	5,7	6,0		
$Ca_3(Si_3O_9)$ - Pseudowollastonite			10,9	5,7
Parawollastonite	8,9	7,2		
Wollastonite – 1A	36,6	14,4		
AlN	3,3	5,4		
SiC	11,1	8,7		

1-[$CaCO_3$+SiO_2+5%$(NH_2)_2CO$]+Al, 50/50; 2-[$CaCO_3$+SiO_2+10%$(NH_2)_2CO$]+Al, 50/50; 3-[$CaCO_3$+SiO_2+ 5%PVA**]+Al, 30/70, 10min, M_p/M_b=1/2; 4-[$CaCO_3$+SiO_2+5%SA*]+Al, 50/50, 10min, M_p/M_b=1/2; *SA – succinic acid, **PVA-polyvinyl alcohol

The greatest amount of wollastonite phase is formed in the sample at the ratio $CaCO_3$:SiO_2=50/50 and in the presence of carbamide. In this case, in the reaction products silicon carbide and aluminium nitride are detected, the amount of the latter increases with the increase of carbamide content. After preliminary avtivation of the system with modifiers the amount of wollastonite in the synthesis products but the content of helenite increases and anorthite is formed.

Conclusions

Thus,the results of the carried out of investigations have shown that mechanochemical treatment of minerals (quartz – SiO_2, calcite – $CaCO_3$) used as components of the charge mixture for SH- synthesis of composition systems contributes, first of all, to the change of kinetic characteristics of the combustion process: the decrease in the induction period of ignition and the increase of combustion rate. The change of combustion temperature is of a complex chatacter due to avtivation of both exothermal reactions (redox reactions) and endothermalones related to formation of complex compounds of the type anorthite, wollastonite and other.

It is stated that the presece of calcite (calcium carbonate) in the charge mixture results in the decrease of combustion rate and temperature at the stage of postprocesses due to decomposition of calcium carbonate with frmation of calcium oxide, carbon oxide or dioxide which, too, take part in reactions of phase formation. Preliminary MCT activates the process of calcium carbonate decomposition resulting in the increase of combustion rate and temperature. Variations of MCT conditions allow to changing the kinetics of the process and provide a more complete realization of initial components of the charge.

A positive effect of the presence of different organic and inorganic additives in the charge which activate the combustion process of the systems on the basis of quartz and calcite mixture is stated. The presence of bound water and ammonia group in a sufficient amount in additive-activators contributes to the increase of combustion temperature, the increase in the amount of a matrix phase (corundum) and aluminium nitride in synthesis products. Specific peculiarities of the effect of succinic acid on the combustion process, namely the increase of combustion kinetic characteristics and temperature of the systems are stated.

The peculiarities of the change of combustion characteristics of multi component systems: combustion rate and temperature increase with the increase in the period of treatment and the number of milling balls are stated. Modification in the process of MCT intensifies the processes of combustion and phase formation during SH-synthesis. The efficiency of modifying MCT manifests it sell in the phase composition of SHS material. In the products of synthesis there form anorthite – Ca (Al_2Si_2O), helenite – Ca_2Al (AlSi) O_7 and wollastonite (pseudo wollastonite) – Ca_3 (Si_3O_9) providing the quality of the final product.

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