

Mechanochemical Activation and Reaction Capacity of SHS-Systems on the Base of Quartz

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Abstract

The influence of different characteristics of mechanochemical activation on changes of structure and energy characteristics of silicon dioxide (quartz) is considered in this work. It is shown that after treatment in mill in the presence of different modifiers, the quartz samples are complex composite formation, composed of crystalline, amorphous and polymeric component, and also contain inclusions of iron and carbon. Polymerized surface layer provides the encapsulation of the energy state of activated particle. Particularities of the technological combustion systems with active and modified quartz are investigated. The using of modifying agents leads to increasing of maximum combustion temperature, increasing of combustion process time as well as the change of phase composition of synthesis products. It is shown that alteration the sizes of synthesized sample (products) we can change the heat dissipation conditions, kinetic of reaction development and temperature in combustion wave. "The process scale" of solid phase combustion at material synthesis appears in change of the phase composition of obtained materials.

Introduction

During the milling of solid bodies in mills of dynamic action in volume and at the particle surface of matter as the result of mechanical action the large variety of defects is occur, which are dramatically changing the reactivity of the substance. The relationship between structural characteristics of solid body and its reaction capacity is the subject of numerous studies [1-5], aimed at understanding of process mechanism and the ability specifically regulate the structure and state of matter, and thus to change its energy characteristics. Defected structure (vacancy defects, dislocations, electro-defective centers, broken links on particle's surface) and voltage of various level, including voltage gradient, arising in shredded particles, have a significant impact on the reactivity of solid bodies.

Except the mechanical changes in milled (and deformed) material the change of electric state of

the system takes place: electron emission in destruction point, electric charge on the surface of deformed particle [1, 6]. The other important factor during the treatment of substance in mill is that the influence on substance has an impact cyclical pattern. In consequence of periodic action of balls the changes in structure of treated matter is occurs by portions, including defect accumulation, particle destruction, defect annihilation and their repartition between volume and surface particle. The consequence of these periodic alterations in structure should be periodicity in alteration of electric charge on the surface particle. As was shown previously [7, 8], occurring electric charge at milling of particles from inorganic matter at concurrent processing of it in mill with organic compounds promote to the polymerization of latest. As the result the formation of composite systems including polymer and inorganic dispersive component. The formation of polymer in the process of mechanical action is also the cyclic process, because along with polymerization the section line break of formed polymer is occur as the result of excited mode, caused by mechanical action of grinding bodies.

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All these facts are essential in the formation of work on influence of processing conditions in mill-activators of different minerals in the presence of organic compounds in order to establish mechanisms of reaction capacity change of milled matters and possibility of stabilization of their activity temporally. As in the process of treatment in mill not only the grinding take place but also chemical reactions of polymerization and inoculation of organic compounds to the active surface of milled particles and thereby modification of surface layers shows the mechanochemical treatment of material and getting the substance of fundamentally new quality.

Upon studying the patterns of activation and modified structure of particles in mechanochemical process, the silica is one of the most favored objects in this field of studies. It shows in full degree the influence of defected structure of various level as well as inception of electric charge on the surface of deformed and destroyed particle, because the silica is piezoelectric, on structural change and alteration of energy state of material. At cooperative processing of quartz with organic compounds should be expected, that electric field which is formed at impulsive mechanical action on the work material will be promote to polymerization, organic component and inoculation of polymer to the surface of quartz particle.

Materials and Experimental

This work was carried out on quartz powder with different purity. It was gangue quartz from Aktas mine field of Zhezkazgan region with purity 98,98% and quartz sand of Kuskudyks mine field with silica content 81,3%, in addition it has 18,7% of microcline, and also different elements, saturating the surface and dissolved in a volume the particles. According to the results of spectrum analysis, it contains from 0,1 to 1,0% of iron, magnesium, calcium, natrium which are may act as active centers in the process of mechanochemical treatment and surface modifying of quartz particles.

As modifiers a different carbonaceous compounds (alcohols, acids, polymers) were used. At the first stage such elements as ethanol - C_2H_5OH , butanol - C_4H_9OH , ethylene glycol - $C_2H_4(OH)_2$, glycerin - $C_3H_5(OH)_3$, acrylic acid - $H_2C=CHCOOH$, polystyrol - $[-CH_2-CH-C_6H_5]_n$. were used in work. Then, the spectrum of used modifiers has been expanded. Carbon and nitrogenous modifying agents were: nitrogen containing compounds acetanilide - C_8H_9ON ,

dicyandiamide - $C_2H_4N_4$, urea - $(NH_2)_2CO$; alcohols: ammonia spirit (i.e. ammonia water) - NH_4OH , manit (or hexahydric alcohol of aliphatic series) - $HOCH_2(CHOH)_4CH_2OH$, polyvinyl alcohol - $(C_2H_3OH)_n$, amber acid - $H_2C_4H_4O_4$, citric acid (hydroxyl tribasic acid with divaricate carbon chair) - $H_3(CO)_3C(OH)_4$, water-containing silicic acid - $H_2SiO_3 \cdot n(H_2O)$ and urea $CO(NH_2)_2$, i.e. carbamide (or in other words diamide of carbonic acid).

For mechanical activation and modification of quartz particles by different organic compounds the planetary-centrifugal mill of dynamic blow grinding action (mechanical reactor) was used. Rotation velocity of platform is 700 r.p.m, rotation velocity of the grinding vessel - 1200 r.p.m. Acceleration rate during the treatment in planetary-centrifugal mill is reached 20 g. The treatment time is varied from 5 to 100 minutes. From powder mixtures of activated quartz with aluminum in stoichiometric ratio of components ($SiO_2+37,5\%Al$) the cylindrical samples with different sizes were formed. For SH-synthesis the aluminum powder of brand IIA4 is used. Diameter of samples is varied from 20 to 59 mm, and the volume - from 6 to 98mm³. The synthesis was conducted by spontaneous ignition in a furnace at heating to 900°C. In synthesis process the temperature and burning speed were fixed with the help of pyrometer by brand ULTIMAX (IRCON).

Before and after mechanical treatment the measurements of dispersity, defectiveness and amount of carbon were conducted in modified quartz powder by standard methods. The sequence of structural change of quartz particles was subjected according to modifier and conditions of mechanochemical treatment.

The particle size (dispersion) of powder is determined on polarization microscope by brand POLAM R-211, which is aimed for the study of crystal objects in transmitted and reflected light. The particles of quartz powder have polycrystalline structure and consist of crystallites with different size. The size of crystallites and also defectiveness degree of dispersed silica and phase composition of synthesized samples were determined by diffractometer "DRON-4M" in cobaltous ($Co - K_{\alpha}$), and also cooper K_{α} -emission in the interval of $2\theta=10^{\circ}-70^{\circ}$. For determination of broadening X-ray lines the value of which is related to the crystallite sizes of substance and lattice strain, the additional X-ray exposure with low speed 1÷2 grad/min in the interval from 40 to 80⁰ were made.

According to results of line width dimension of quartz for interplanar distance $1,98\text{\AA}$, where there is no prevailing direction influence, the sizes of crystallites (L) were calculated with an accuracy $\pm (8\div 10\%)$.

Electron microscopic analysis of modified quartz particles was carried out by electron transmission microscope Jem -100 CX; U-100 kv. For investigation the samples were prepared by dry preparation method. As prototype unmodified silica the particles rock crystals which were porphyzied in agate mortar without dispersion medium were investigated.

Results and discussion

In the first place, while processing of quartz in mill-activator the pounding of particles and their saturation by defects is occur, whose presence changes the energy state of the material, and consequently, its chemical activity. The deficiency of silica particles after mechanical treatment was assessed in accordance with X-ray line broadening on half-height of peak. According to measurement results on line broadening of quartz for interplanar distance $1,98\text{\AA}$, where there is no prevailing direction influence, the crystallite sizes were calculated. The measurement results (figure 1) shown that as the line width (FWHM), and crystallite size (L) of quartz with the time of treatment in mechanical reactor are change not linearly.

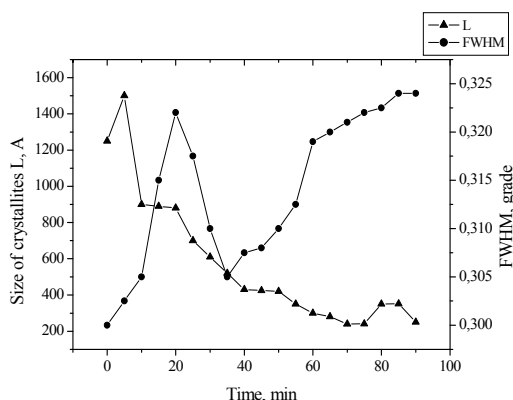


Fig. 1. The alteration of X-ray line broadening (FWHM) and crystallite size (L) of quartz powder particles from time of mechanochemical treatment

Here we can observe the periodicity in increase and decrease of these characteristics, ie in structure imperfection of particles. The observed periodicity reflects the process of material dispergation and formation of defective structure (accumulation and defect annihilation) in the particles. The line

broadening is a summary reflection of dispersion increase, defect accumulation and surface amorphization.

The obtained regularities also reveal the number of extreme points, reflecting the peculiarities of structural changes in quartz. So, during the treatment 15÷20 minutes of quartz a considerable increase of X-ray line broadening and inhibition in change of crystallite dimension is observed, that may be connected with increasing of particle dispersion, accumulation of surface defects and, conversely, with regeneration of bulk defects or release them to the surface. Time duration of treatment is 30÷40 minutes, judging by decrease intensity of X-ray broadening and size of crystallites are characterized by considerable volume changes in structure of dispersible material. At that the recombination of surface defects and agglomeration of particles is possible. Based upon presented measurement results of these characteristics, a longer treatment of quartz (from 50 minutes and more) leads to the size reduction of crystallites and structure change and condition of surface particle layers in condition of dispersion reduction due to agglomeration of powder. So, the treatment during 20 minutes provides the most significant changes in structure and especially surface layer of silica particles.

Thus, as shown previously [9, 10] and scientifically confirmed by results [11] the most important factor of the mechanical treatment process is the periodicity of structural changes in volume and on the surface of milled particles of silica, where the broken links plays an important role [12, 13]. The broken links are active centers of chemical reaction development between milled silica and organic compounds, presented in treated mixture. The result of interaction between components of milled mixture is a change in dispersity of the material.

At the first stage of work the investigations with using as modifiers of different alcohols (one-, two- and three atoms) are carried out. As known [2], the alcohols are surface-active materials, which actively promote to pounding. The most effective action in this context is monoatomic alcohols. The dispersity of quartz powder treated at the presence of (5 mass.%) ethanol (C_2H_5OH) and butanol (C_4H_9OH), significantly increased, and dispersion in particles size is decreased (figure 2). At that, differential characteristic of particles, treated in the presence of butanol is a slight increasing of particle size of main fraction, constituting more that 50% of powder volume.

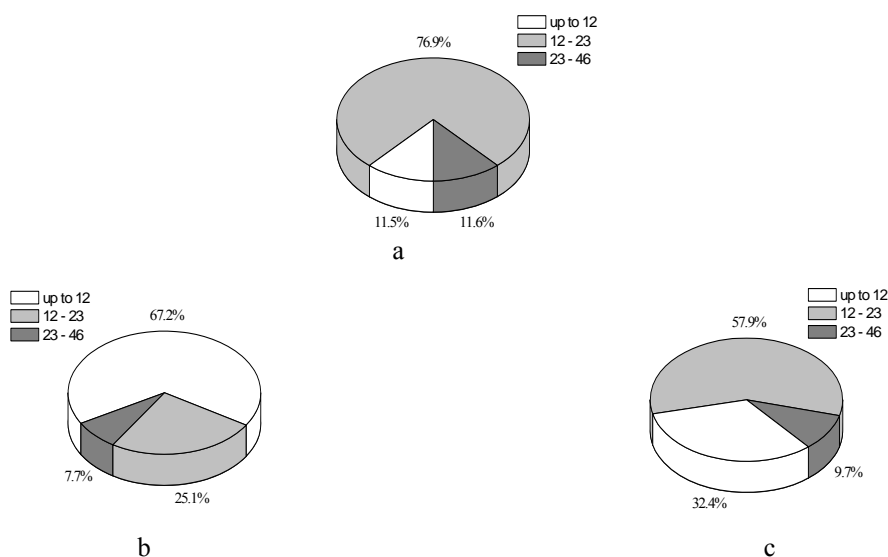


Fig. 2. Particle distribution according to the sizes (in μm) after 10 minutes of pounding for quartz (a) and silica treated by ethanol (b) and butanol (c)

A similar situation takes place when using as additive ethylene glycol ($\text{C}_2\text{H}_4(\text{OH})_2$ – diatomic alcohol) and glycerin ($\text{C}_3\text{H}_5(\text{OH})_3$ – triatomic alcohol). Some particle coarsening and increasing of powder polydispersity after 20÷25 minutes of pounding with these modifiers may serve as indirect evidence of changes in their size by modification (increasing) of surface layers. The increasing of milling time more than 40 minutes leads to coagulation of small particles. Fractional composition of modified powder after long-term treatment is more monodisperse, i.e. dispersal in particle size becomes more smaller, than for unmodified quartz.

The acrylic acid ($\text{H}_2\text{C}=\text{CH}-\text{COOH}$) and styrole ($\text{CH}_2-\text{CH}-\text{C}_6\text{H}_5$) are known [14; 15], as one of the most active modifiers of inorganic materials.

Already in poor mechanical action (galling in pounder) the acrylic acid and styrole are polymerized.

At intensive mechanical chafing the polystyrol is exposed to destruction and re-polymerization [14, 16]. As the result of mechanochemical treatment the quartz powder treated with acrylic acid and polystyrol is characterized by changes not only structure, but and morphology of particles, and possibly the presence of polymerized layer on the particle's surface. It was obtained that in the process of dispersion of modified particles (figure 3) their size was increased, respectively to 90 and 120 micron, compared with quartz, ground up without modifier, when the largest particles did not exceed 50 micron.

Thus, pounding of quartz in the presence of various organic mixtures has a significant impact on the pounding process, dispersion degree of the material and transformation of structure of surface layers of the particles.

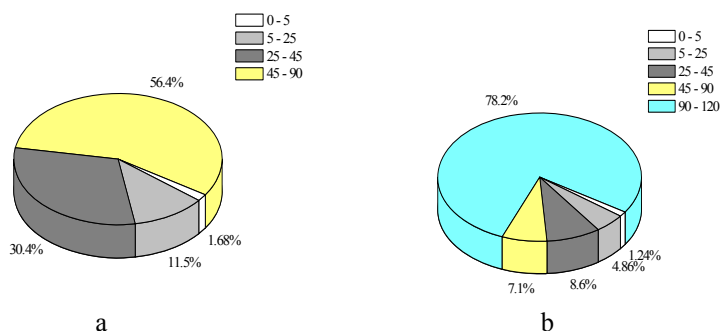


Fig. 3. Particle distribution by sizes (in μm) for quartz, treated with acrylic acid (a) and in the presence of polystyrol (b)

The results of X-ray structure analysis showed that, the presence of organic modifier affects on change of defective structure in particle volume, i.e. in quartz core. The organic formations on the particle surface do not fixed by X-ray diffraction method, in this case they are “clear” for it. It was obtained that (figure 4) the presence of modifiers, especially acrylic acid, after 20 minutes of treatment clearly promote to the

reduction of crystallite sizes [17], i.e. increase of volume defectiveness of samples and consequently change its energy state. The quartz milled in the presence of polystyrol, in a greater degree shows X-ray line broadening, but in a less degree the change of crystalline size. Therefore, by changing the modifying organic mixture, we can essentially influence on changing of internal structure of dispersible inorganic material.

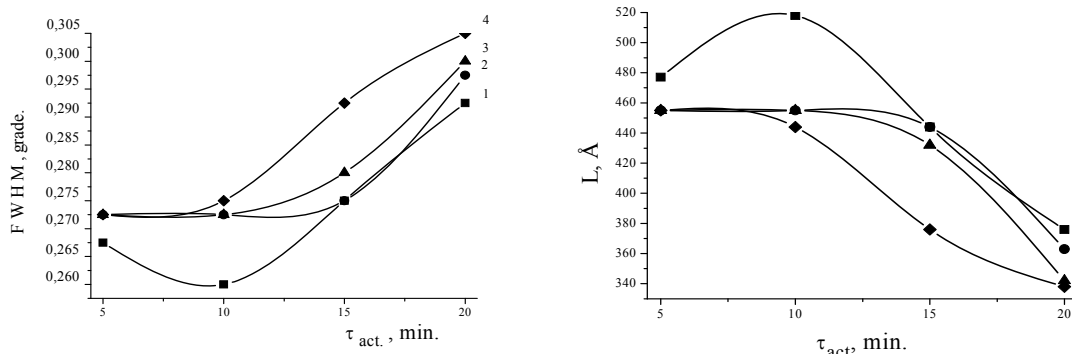


Fig. 4. The alteration of X-ray line width (FWHM) and size of crystallites (L) from time of quartz treatment, activated without (1) and in the presence of modifiers: ethanol (2), butanol (3), acrylic acid (4) and polystyrol (5)

Electron-microscopic analysis is the most informative method for studying of structure and high dispersive particles. Even after the treatment of silica in planetary centrifugal mill with monoatomic alcohols the morphology of particles undergoes significant changes [18]. The using of butanol as dispersion agent to milled material, the loose and layered structure of particle surfaces is

visible (figure 5) in which there are more dense inclusions. These inclusions are particles of iron or its compounds, which are in the beating process, are rubbed from vessel surface and grinding balls and penetrates into silica surface. Especially such sections are clearly visible for the material, which is milled in a mill without modifier (i.e. dry).

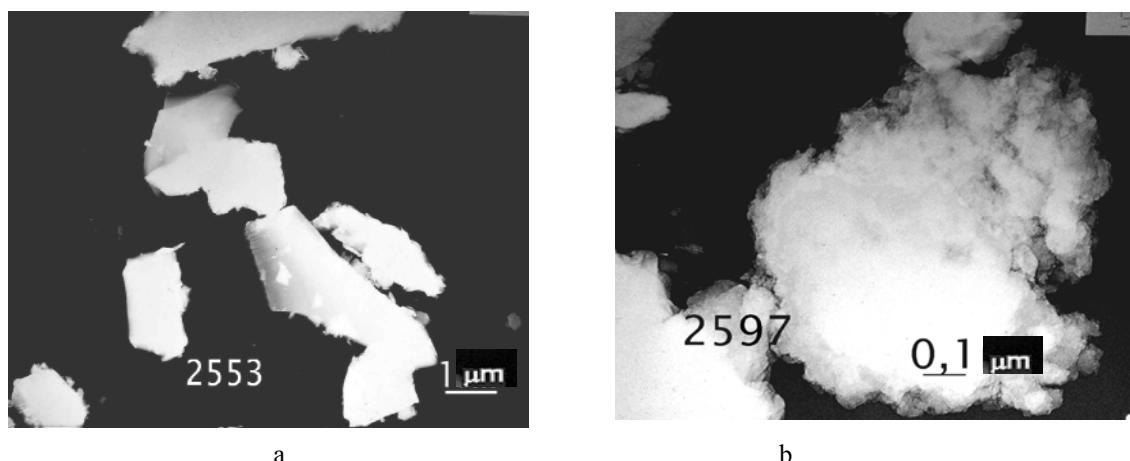


Fig. 5. Electron micrographs of quartz powder particles, in initial state (a) and dispersed in centrifugal planetary mill in the presence of butyl alcohols (b)

The surface layer of modified silica particle is a multi-layered formation with different density structure, rich by carbon, as evidenced by electron

micro diffraction results, which were obtained from particle surface. According the results of electron micro diffraction we can trace the process of

stepwise transformation of quartz particles (figure 6a) to the microcomposite material, which contains the particles with partially amorphized (figure 6b)

and modified surface, up to formation of dense carbon structures on the quartz surface (figure 6c) which is specifically treated with butyl alcohol.

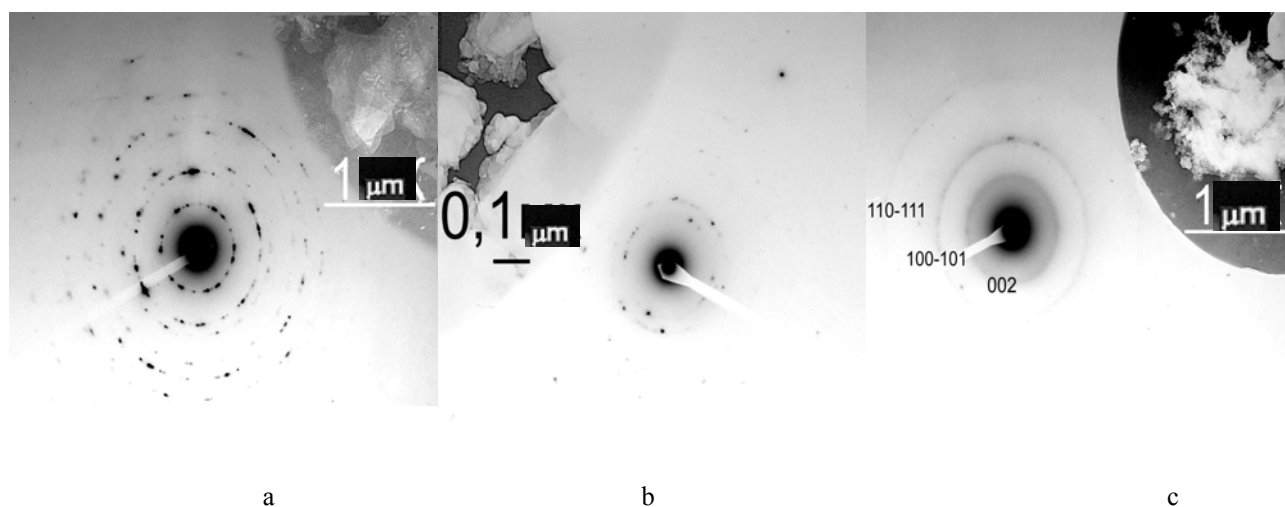


Fig. 6. Electronograms of quartz in initial (a), activated (b) and modified (c) condition

When replacing the monoatomic alcohols to polyatomic at dispersion of quartz the particle shape and their structure are significantly change. The specific feature of modified material in such situation is a formation of spherical particles and

their dendroid aggregates, that is particular evident when we use the glycerol (figure 7a). With increasing of processing time the particle size decreases, and the conglomerates of high-dispersive formations is become more complex.

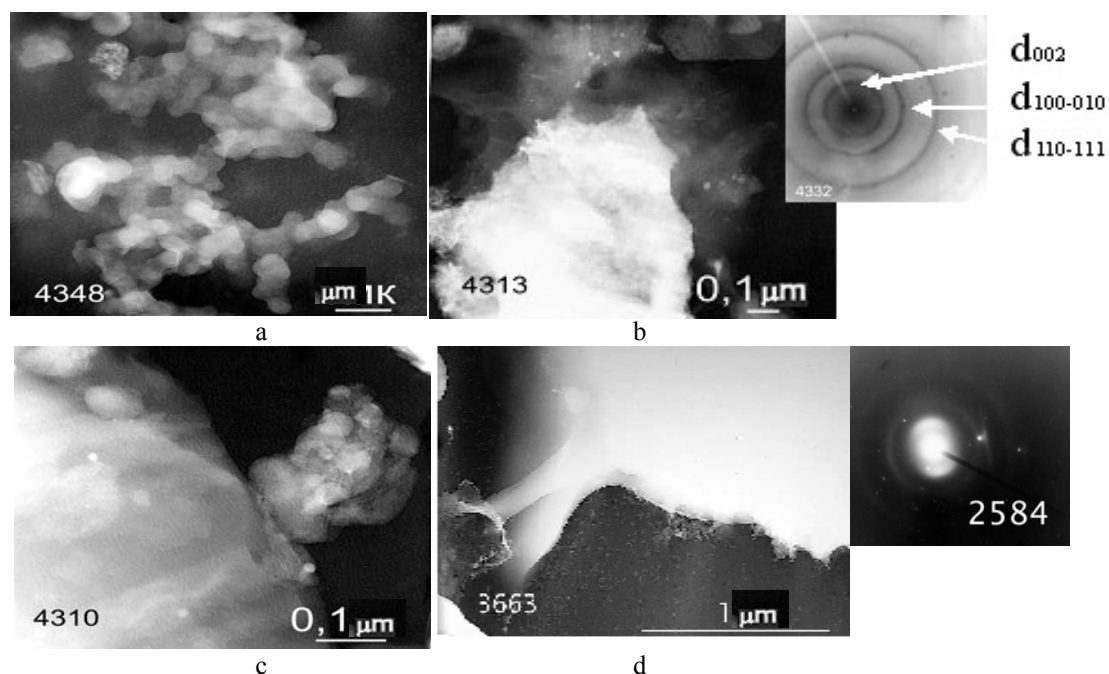


Fig. 7. Electron micrographs and electron modification of quartz particles, modified at combined mechanical treatment with glycerin (a), acrylic acid (b) and polystyrol (c, d)

The modification of quartz particles by acrylic acid during the process of mechanical treatment leads to formation on the surface of a dense, fairly

homogeneous film and also the presence of high-dispersive crystallites in surface polymeric layer. There is also the formation of homopolymer,

unrelated to the quartz surface. Diffraction pattern indicates the formation of quartz organic composites in such situation (figure 7b). The most compact structure of the polymeric layer on quartz surface is formed when we use polystyrol as modifier. In addition, on the surface of these particles the different nanostructural formations are formed, grafted to the surface (figure 7 c, d).

Thus, in the process of mechanochemical quartz treatment with organic compounds the complex multi-stage formation process of carbonaceous structures on the particle surface is occur, which can be considered according to [19], as the result of graft to radical centers ($\equiv \text{Si}^\cdot$ и $\equiv \text{SiO}^\cdot$), arising on the surface of split groups of disrupt organic compounds. The degree and form of carbonaceous of silica surface is determined by form of used modifier.

The number of fixed carbon in modified quartz is determined by absorptive weight method. Measurement results are presented in table 1. With the same weight of input modifier and the same time of treatment the maximum number of fixed carbon – 2,6% was found in the samples with polystyrol, showed maximal variety of structural forms on the surface of modified particle [11].131

Table 1

The content of carbon and iron in modified surface layer of silica particle after mechanochemical treatment with different modifiers.

Material	$\tau_{\text{act.}}$, min.	C,%	Fe,%
quartz (int)		0,08	0,05
quartz (act)	10	0,08	2,32
quartz (акт)	20	0,08	3,34
quartz + C ₂ H ₅ OH (5 %)	20	1,06	11,62
quartz + C ₄ H ₉ OH (5 %)	20	1,76	14,86
quartz + C ₂ H ₄ (OH) ₂ (5 %)	20	1,45	6,78
quartz + C ₃ H ₅ (OH) ₃ (5 %)	20	1,53	4,94
quartz + AA* (5 %)	20	2,03	5,62
quartz + PS** (5 %)	20	2,60	7,08

*AA – acrylic acid, **PS – polystyrol.

Except the data on carbon content in volume of modified silica, in table there are results of X-ray analysis of iron content in quartz after its mechanochemical treatment. Iron is the second element, introduced to the silica during its milling, and actively participates in structurization of surface layer of particles of modified quartz

powder. The amount of iron in treated quartz varies from form of used modifier. The highest content of iron is found in samples, milled in the presence of alcohols and especially with using of butanol.

So, electron-microscopic images of quartz particles, modified at mechanochemical treatment with different organic admixtures, clearly demonstrate the formation of nanosized originations on the particle surface. Modified surface layers may have porous as well as dense structure and in some cases they are absolutely new formations, which can be attributed to tubular forms. In formation of such structures are participate quartz, oxygen, carbon and iron. Eventually, quartz particles, modified in the process of mechanochemical treatment have complex structure. There are reductions on the particle surface: carbon and iron installed in polymerized surface layer, which provides not only encapsulation of energy state of the activated particle but also prevents from early oxidation the nanosized iron staining. So, modified in mechanochemical treatment quartz particle is a complex composite, consisting of crystalline, amorphous, and polymer component and contains inclusions of iron and carbon.

During the using of such quartz powder as reagent for synthesis of ceramic materials in SHS regime, each of components of composite particles will be participate in the process of technological combustion. The first experiments with quartz, activated and modified by monoatomic alcohols at a ratio of powder mass to the mass of balls $M_p/M_b=1/2$, have shown a significant increase of combustion temperature it depends from mechanochemical treatment time and used modifier (figure 8) is a reflection of change of reaction capacity of the material due to conditions of its treatment. The most significant increase of combustion temperature was fixed after 15-20 minutes of activation, which correspond to the maximum change of defective structure of particles, according to the results of X-ray spectrum analysis (figure 1).

When we used such complex compounds (polystyrol and acrylic acid) as modifier, we have found that combustion temperature reaches 2000°C and higher, and the combustion process has a number of specific features [20]. First of all, in development of combustion some stages are fixed it may be related to structural features of modified particles, namely with presence of particles of iron and carbon in surface layer.

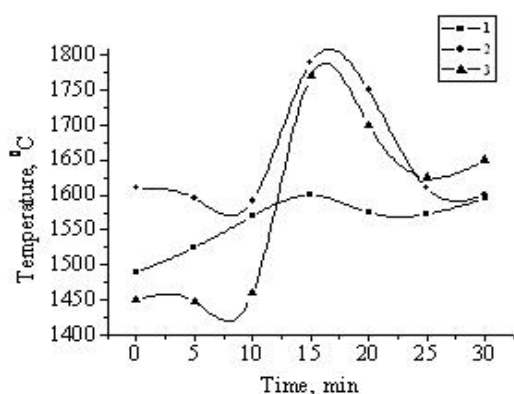
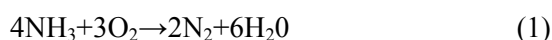


Fig. 8. The dependence of combustion temperature of system $\text{SiO}_2 + 37,5\% \text{Al}$ from time of mechanochemical treatment of quartz without modifiers (1), with ethanol (2) and with butanol (3)

The one factor is also has drawn attention – the intensification of combustion process at the presence of bound water in modified surface layer of particle. Special investigations on silica from Kuskud minefield with modifiers containing various numbers of bound water and also ammoniac groups were dedicated to this factor. Figure 9 shows the thermograms of combustion samples of system ($\text{SiO}_2 + 37,5\% \text{Al}$) with quartz, activated with modifiers, which contains ammoniac group. It should be noted, that the combustion temperature of system with quartz of Kuskud minefield is much lower, than with quartz of Aktas minefield because it contains more mixtures.

Thermograms of combustion have shown that depending on modifier all parameters of combustion are change: induction period, combustion rate, maximum combustion temperature and thermal regime at the stage of postprocess. These changes are associated due to the fact that for all used nitrogenous additives the elimination at heating of ammonium molecular is characterized. It is known, that at heating the ammonium is exhibit the reducing properties. So, it burns in oxygen atmosphere, forming water and nitrogen.



The strongest effect from number of used nitrogenous additives showed the presence in sample of ammonia water and urea, which is at heating to $150\text{--}160^\circ\text{C}$ and dissolved with the formation of biuret - $\text{H}_2\text{NCONHCONH}_2$, NH_3 and CO_2 , i.e. the decomposition products contain

ammonia and carbon dioxide. Then the oxidation of ammonia according the above formula with formation of nitrogen and water is occurring. Dicyandiamide $\text{C}_2\text{H}_4\text{N}_4$ at heating higher the combustion temperature 209°C is dissolved with separation of ammonia and formation of melamine ($\text{HN}=\text{CNCN}$). Acetanilide $\text{C}_8\text{H}_9\text{ON}$ (or $\text{C}_6\text{H}_5\text{NH}(\text{C}_2\text{H}_3\text{O})$) melts at $114,3^\circ\text{C}$, and boils without decomposition at 305°C .

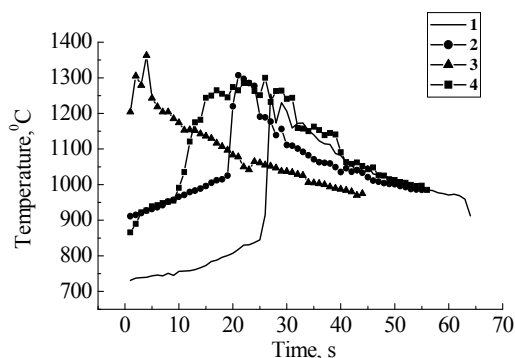


Fig. 9. Thermograms of quartz combustion with aluminum: without additives (1) and in the presence of 5% of ammonia water NH_4OH (2), urea ($\text{NH}_2)_2\text{CO}$ (3) and dicyandiamide $\text{C}_2\text{H}_4\text{N}_4$ (4)

At using of acids and alcohols as activated additive-modifiers it was found, that the kinetic of the process is sharply increase: induction period is decrease, speed of starting increase, as the result the combustion temperature is increase (figure 10). The greatest effect was obtained at the presence of water silicic acid and polyvinyl alcohol, i.e. compounds containing a bound water in large number at, which is at heating (above $200\text{--}400^\circ\text{C}$) is separate.

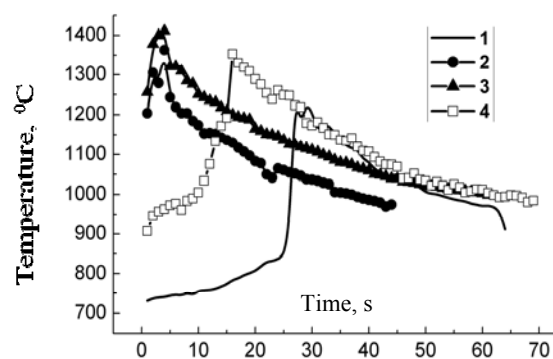
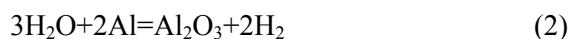


Fig. 10. Thermograms of quartz combustion with aluminum without additives (1) and at the presence of 5% water silicic acid $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (2), polyvinyl alcohol $(\text{C}_2\text{H}_3\text{OH})_n$ (3) and amber acid $\text{C}_4\text{H}_6\text{O}_4$ (4)

If at the heating of amber acid the one molecule of water is separated and anhydride of amber acid is formed (in the form of five-membered ring), so at heating of polyvinyl alcohol and water silicic acid the n -number of water is separated. Accordingly, the segment base and increasing of combustion temperature is occur. Thus, conclusion about positive role of bound water, presented in mixture components, on combustion process is appear. The presence of water leads to interaction of it with aluminum and formation of hydrogen and aluminum oxide.



The reaction proceeding with the release of large number of heat, and formed hydrogen, is strong reducing agent, react with silicon oxide and recovers silicon in accordance with equation



Figure 11 shows the integrated data on dependence of maximal combustion temperature of the type of used modifiers. Curve $T_{\max} = f(M)$ shows the temperature rise: 1 – the content of nitrogen (ammonium group) and the presence of OH group in additive-modificator.

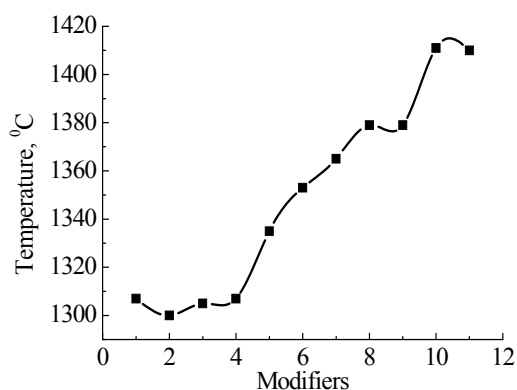


Fig. 11. The dependence of maximum combustion temperature of system $\text{Al} + \text{SiO}_2$ without (1) and at the presence of additives -combustion activators: 2 - amber acid+ammonia water, 3 - ammonia water, 4 - amber acid, 5 - acetanilide, 6 - dicyandiamide, 7 - citric acid, 8 - manite, 9 - water silicic acid, 10 - urea, 11 - polyvinyl alcohol

We should pay special attention to the results of bound water, which presented in additive-modificator. With increasing of its number the combustion process is intensified, as the

consequence of aluminum oxidation and at that the formation of atomic hydrogen, which is act as active reducing agent of silicon dioxide.

Thus, by mechanochemical activation and modification of surface layers of disperse particles we can purposefully influence on the development of combustion process, its thermo kinetic characteristics, that finally may realize in phase composition and properties of synthesized material.

Also it should be noted, that powder consisting of modified particles is a homogeneous mixture with normally distributed in volume of inorganic and organic component, with inclusions of carbon and iron in surface layer of particles. Such uniform structure predetermines the possibility of stationary development of combustion process. External view of synthesized samples (figure 12), which were obtained during combustion of mixture ($\text{SiO}_2 + 37,5\% \text{Al}$) at 1000°C with quartz in different initial condition concern that the modification of inorganic oxidizer provides uniformity in structure and phase composition of synthesized sample. This fact indirectly reflects the stationary of combustion process, which is critical moment when selecting the technological parameters of synthesis of SHS – products. But the using of activated quartz without modifiers in SHS-systems, conversely, enhances the effect of thermal explosion. Propagation of combustion wave from the center of sample is accompanied by exteriorly significant difference in combustion products in different parts on sample section. This difference was confirmed by the results of X-ray analysis.

Except the above, scale factor is the effective influence method on combustion process of synthesized material. If we change the sizes of synthesized sample (product) we can change heat dissipation conditions, kinetic of reaction development and temperature in combustion wave. Finally, all these factors have an impact on phase composition, structure and properties of the produced materials. Scale effect for SHS-materials, primarily associated with the presence of gas-phase reaction products that enhance the defect structure.

For activated and modified systems the scale effect is more pronounced. Figure 13 shows the experimental data, which were obtained at combustion (900°C) of system with quartz from Aktas minefield. From presented results suggest that pre-activation contributes to significant increase of combustion temperature of samples with small size.

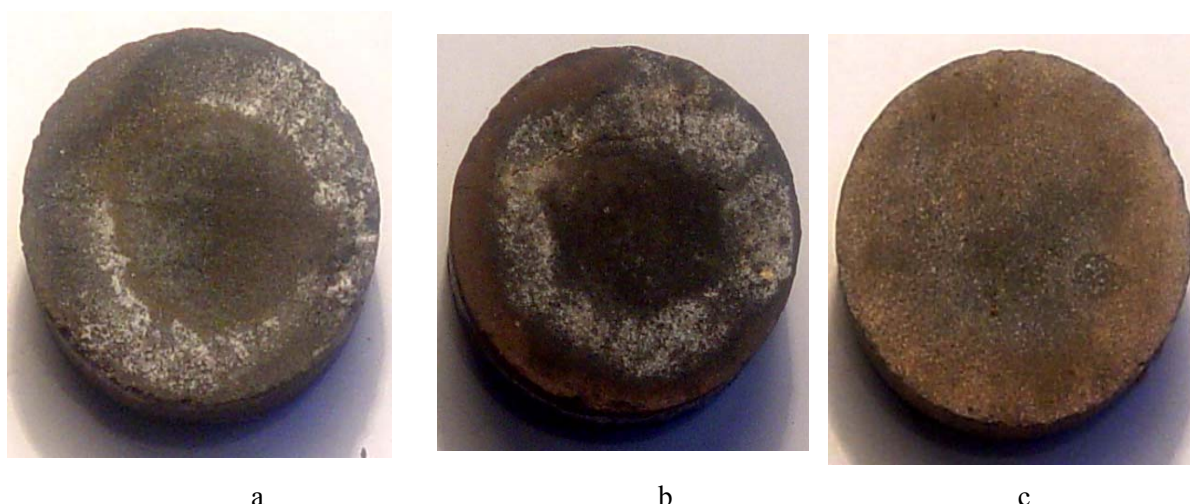


Fig. 12. External view of samples, synthesized on the base of non-active (a), activated (b) and modified (c) quartz

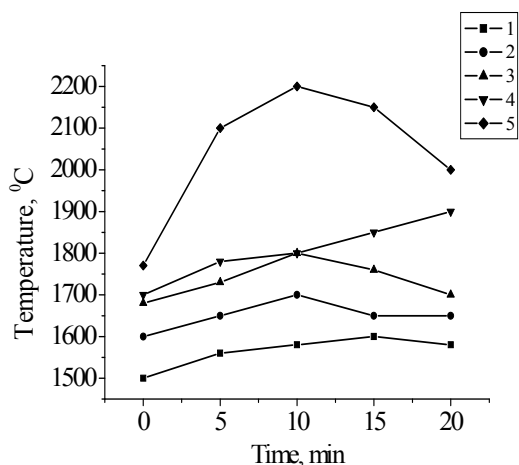


Fig. 13. The dependence of combustion temperature of samples (37,5Al%+SiO₂) from time of mechanochemical treatment of quartz. Sample volume: 1 – 6 cm³, 2,4 – 49 cm³, 3,5 – 98 cm³. Activation without (3) and with polystyrol (4, 5). The temperature of heat burner 900°C.

At sample volume 3 cm³ after 10 minutes of silica activation the combustion temperature increases up to 1800°C. In case with quartz, modified by polystyrol, the scale effect is most pronounced after 5-10 minutes, providing increase of combustion temperature up to 2200°C. With more prolonged treatment of quartz (until 20 minutes) the role of size factor in development of combustion process decreases. In this case, the role of structural changes in material as the result of preliminary of mechanochemical treatment is more prolonged.

The scale-effect in SHS systems with activated quartz is evident not only in change of combustion temperature but also in final result of synthesis i.e. in reaction products. It is established that on samples with big size in maximal degree the recovery of Si is occur, and the formation of sialon which is involved in the synthesis of nitrogen from the air [20]. The content of sialon in large-scale samples contained up to 18%. This fact is important because it indicates that in dependence of volume of sample the kinetic of combustion, diffusion rate and sample structure are change. Significant contribution in formation of phases and structure of such samples are gas-phase reactions.

During investigation of scale factor on samples with silica from Kuskudyk minefield it was also registered that in dependence of sizes of synthesized sample the thermokinetic characteristics of combustion process and phase composition of obtained products are change. In table 2 the results of phase analysis of synthesized samples on the base of quartz with scale factor are presented. With increasing of sample volume the initial components in combustion reaction are fully realized, mullite and also FeAl₃Si₂, FeSi₂ и AlN are formed.

Thus, the sizes of synthesized samples (scale factor) play an important role in changing of combustion temperature and phase composition of synthesized material. This dependence is manifested most significantly for activated and modified mineral component of SHS system as the result of mechanochemical treatment.

Table 2

Phase composition in combustion products of SiO₂+37,5%Al system in dependence of size (d/h) of synthesized samples and type of modifiers at 20 min of mechanochemical treatment.

Phases	Phase content,%								
	Samples								
	1	2	3	4	5	6	7	8	9
Al ₂ O ₃	48,4	59,0	53,9	67,4	49,4	64,0	61,7	51,2	62
Si	12,9	21,9	18,9	19,0	15,4	20,7	22,3	12,3	15,2
Al	12,2	4,2	5,1	3,5	16,7	2,6	0,3	9,0	3,5
SiO ₂	24,7	2,6	2,8	8,2	3,9	0,9	1,6	18,1	0,7
3Al ₂ O ₃ 2SiO ₂		7,9	7,8		7,5	4,8	7,8		7,1
FeAl ₃ Si ₂	1,8	3,5	2,5	10,1	5,2	5,6	3,0	2,6	3,7
AlN			7,5					7,8	5,1
FeSi ₂		1,0	1,6	1,8	1,6	1,6	3,2		2,7
Ca(Al ₂ Si ₂ O ₈)					0,3				

1-(SiO₂+Al), 20/20; 2-(SiO₂+ Al),30/30; 3-(SiO₂+ Al),50/25; 4-(SiO₂+ Al+ 5%AA*), 20/20;
 5-(SiO₂+ Al+ 5%AA), 30/30; 6-(SiO₂+ Al+5%AA), 50/25; 7-(SiO₂+Al+5%AA), 50/50;
 8-(SiO₂+ Al+ 5%PVA**), 20/20; 9-((SiO₂+Al+5%PVA**), 50/25; *AA-amber acid, **PVA-polyvinyl alcohol

Conclusion

The experiments shown that, synthesized at mechanochemical treatment material on the base of quartz is a composition powder system, the multilayered surface formations of particle which have nanosized scale and differ by heterogeneity of constitutive elements. The variety of combinations of surface structures, the main parts of which are polymers, iron and carbon were found. It was established that, nanostructured surface layers of modified silica particles with participation of iron and carbon changing the kinetic process, providing greater combustion temperature. According to the X-ray analysis the most significant increase of combustion temperature was fixed after 15-20 minutes of activation, which correspond to the maximum change of defective structure of particle.

It is shown that the choice of charge modifiers is determined by their active components, including bound water and nitrogen except carbon. The water molecules interacting with aluminum provides the formation of hydrogen. If time of mechanochemical treatment is more, so the probability of active monoatomic hydrogen obtaining is bigger, which actively participate in combustion process. Nitridation of system contribute to the formation of nitrides, which increase the combustion temperature of mixture.

The effective influence method on combustion process of synthesized material is also scale (dimensional) factor. If we change sizes of

synthesized sample (material) we can change the heat dissipation conditions, kinetic of reaction development and temperature in combustion wave. Finally, this affects on phase composition of synthesized material, and consequently on its properties.

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