SHS of Oxide Systems Based on the “Mechano-Chemical” Quartz Modified by Organometallic Compounds

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Abstract
The differences of the effects of mechanical substance pre-activation in the mills with divers force effect schemes on the self-propagating high temperature synthesis (SHS) of the SiO$_2$ + 37.5 % Al system are shown. The power saturation of activated material is determined by particle defect intensity and effects on the thermal and physical characteristics of the material. The variations of activated material state are estimated referring on the variations of dilatometry curve paths. The effects of activation time on the temperature of sample self-ignition in the furnace, combustion temperature and completeness of the quartz reaction with aluminum are determined. The enhancing effects of organic modificators of quartz particle surfaces on the further SH synthesis development are shown.

Introduction

The dispersion process of the quartz in the mills results in its profound microstructure and morphology modifications. In grinding processes there are occurred both the increase of particle surface area and the modification of surface layer state, as well as the available defects are gaining (vacancies, dislocations, disclinations) in a particle volume; also, in the points of bound breakage when particles are fractured there are formed divers reaction centers [1]. In cases of mechanical processing of powder mixtures containing both inorganic and organic compounds in the contact points of divers material particles the pressure is achieving up to 10$^9$ Pa. It results in the diffusion rates being increased by few orders of magnitude and surface particle layers are saturated with atoms of other elements as well as there are formed new chemical compounds. Such interactions result in the modification of particle surface up to more active state or in capsuling them in the shell of new compounds. A quite prolonged processing may cause the particle welding (sintering) of two divers materials and formation of one new compound. This is a so-called process of mechanical doping which is quite thoroughly studied in the overview paper [2]. First stage of such process development is particularly interesting for us because it is related with the transformation of surface layer structure.

The controlled structure and conditions modifications of particle surfaces of the powder materials have considerable importance for producing of them by SHS synthesis divers new compounds. It is known [3] that the thermodynamics and kinetics of redox reactions are depending on the powder dispersion degree. This dependence shows an extreme characteristics, i.e. the maximum reaction velocity is observed for certain sizes of reagent particles. It is conditioned by that the reactions are initiated from the particle surface therefore the optimum reagent contact and conditions of surface layers of interacting particles will determine velocity and completeness of process development. The pre-processing of SHS-mixture components enables to obtain both optimum material dispersion degree and more perfect reactivity state of the particle surface.

It is known [4] that to produce fine dispersions of inorganic fillers for composite polymer-ceramic materials in process of powder grinding there are used divers organic additions whose reactions with powders result in formation of thin layers of organic and organo-metallic compounds on the solid particle surfaces. The compositions and structure of such layers are depending both on the particle materials and mechanical processing conditions. In process of further heating such organic formations are enable to be de-
Experimental

The dilatometry analysis is one of the most structure-sensitive method of the material condition determination. The thermal dilatation as well as other thermo-physical characteristics of the substances are readily responding to minute changes of phonon and electron sub-systems of crystal lattice of the solid substances. The defects accumulated by the material in result of mechanical processing alter the spectrum of phonon variations and electron density in the defect sections of crystal lattice. The both factors are causing the alterations of bounding strength between the structure elements that, effects on the intensity of the thermal sample dilatation. The comparison of dilatometry measure results, i.e. variations of sample sizes with temperature $\Delta L/L = f (T \, ^{\circ}C)$ before and after mechanical material activation enables to estimate the degree of powder mixture activation. In this paper the dilatometry analysis was carried out with programmed automate dilatometer-recorder of company «ORTON».

SHS synthesis was carried out with the $\text{SiO}_2 + \text{Al}$ samples having stoichiometrical composition. The quartz and its mixtures with aluminum were subjected to the mechanical activation in two mills: centrifuge and planetary-centrifuge ones in conditions of equal powder masses and grinding balls ratios. In first mill the shifts of grinding balls were limited and force excitation of processed powder came mainly to its grinding, i.e. the material was subjected to the shifting deformation. In second mill with free ball movements under the effects of centrifuge forces the processed powder was subjected to the impact and friction effects, i.e. to the compressive and shifting deformations. Because the differences of force effect schemes the structure modifications of the particles milled in the first and second mills must be different ones and so thus, the activated states of the material, even at the same value of accumulated power whose values were determined by thermo-graphical method, shouldn’t be equal values that is confirmed by dilatometry curves.

Results and discussion

The dilatometry curves of the quartz show a particular characteristics and consist of three sections with divers coefficients of linear thermal dilatation (LTDC). The heating was carried out up to 1000$^{\circ}$C. First curve section shows the dilatation of $\alpha$-quartz, third curve section shows $\beta$-quartz dilatation and second curve section with the LTDC considerably exceeding both other ones is conforming to the state of transition preparation $\alpha \rightarrow \beta$ for which the bonding strength decrease is specific that is predetermining factor of structure modification from the triangle lattice to the hexagonal one. On the Figs.1 and 2 the quartz dilatometry curves in its initial, equilibrium after burning and activated states at different exposure duration times in two mills are presented. From these figures it follows that after the quartz processing in the centrifuge and planetary-centrifuge mills its thermal and physical characteristics (the intensity and thermal dilatation degree) vary in different manner depending both on the exposure duration and heating temperature. After quartz processing in the centrifuge mill during up to 12 minutes period its dilatation degree, especially in third temperature range (over 500$^{\circ}$C), is decreasing and on the contrary it is increasing for the quartz activated during 20 minutes period and more in comparison with the samples in their initial and burned states (Fig. 1). The quartz mechani-
cally processed during 13-18 minutes is of particular interest. For it the section of dilatometry curve over 500°C shows the alternation (periodicity) of dilatation variations ↔ compression, i.e. the path of this curve section isn’t monotonic. In the repeated heating of the same sample the path of thermal dilatation curve becomes regular (fair) and this curve is located in the intermediate position regarding to the dilatometry curve of activated (15 minutes) quartz. So thus, the quartz conditions obtained by 15 minutes (more refined: from 13 to 18 minutes) processing in the centrifuge mill are very particular because it shows a duality specific for material activated during shorter or longer time period. Therefore the path of the curve Δ L/L = f (T °C) is varying within these two condition range. After quartz milling during 3 minutes and more in the planetary-centrifuge mill there is occurred only the decrease of intensity and thermal dilatation degree (Fig. 2). However the dependence of these values on the processing duration is remained as a non-linear one. The most important variation of the curve path is occurred after 20 minutes period of activation.

On the Fig. 3 there are presented the dependences of LTDC values (α) on the activation periods (τ_act.) for three temperature ranges of sample heating (α - quartz, α → β transition pre-conditions and β - quartz). The mechanical pre-activation is showed in the most degree at the stage of α → β transition pre-conditions. Depending on the activation period the LTDC within 400 - 500°C range varies by over one order of magnitude both in direction to the decrease and to the increase. At lower and higher temperatures such variations achieve few units and unit fractions. Thus, the mechanical pre-processing is showed in more intensive degree in the variations of material conditions and properties at temperatures preceding polymorph transformation of the substance. This established fact is very important to determine optima conditions of further synthesis carrying-out of pre-activated materials and to select optimum duration period of its mechanical processing. The latter follows from the fact that for the quartz processed in the centrifuge mill during 15 minutes period there is occurred a substantial increase of the LTDC value. The structure modifications of quartz particles during 20 minutes period sharply reduce their thermal dilatation and the further dispersion process only is enhancing the thermal dilatation intensity increase. For material processed in the planetary-centrifuge mill, on the curves α = f (τ_act) there is observed only sole extreme point which falls on the 20 minutes period of activation.

After particle pre-activation conforming both to the thermo-graphical and dilatometry analyses data the temperature of α → β transition; and such variations occur within 90 - 150°C range depending on the exposure time and show non-linear characteristics.

So thus, the quartz processing in the dynamic mills of centrifuge and planetary-centrifuge types results in the structure modifications of the particle surfaces and their volumes showing modifications of their properties in their further heating but they aren’t equally meaning ones. In the centrifuge mill the SiO2 particles in more significant manner are subjected to shifting deformation (milling) and in the planetary-centrifuge mill - to the compression (impact). In first case there is occurred a more intensive grinding and amorphization of particle surfaces layers; in second case the more intensive volume modifications of particle structure are occurred. The amorphization of quartz parti-
SHS synthesis was carried out using the pre-activated quartz and its mixtures with aluminum of stoichiometric composition. The effects of activation duration on the self-ignition, combustion temperature and reaction completeness are determined by phase compositions of synthesis products at divers temperatures of furnace heating (Table 1). After SiO₂ activation in the centrifuge and planetary-centrifuge mills the furnace temperature assuring the sample self-ignition is decreased from 670°C down to 600 and 570°C respectively, the more complete running-out of redox process being achieved comparing with activated oxide use. The increase of furnace heating temperature up to 850 and 900°C assures respectively more complete silicon reduction (up to 24%). The further furnace temperature increase results in the alteration of the combustion stability. It is running conforming to the thermal explosion type. It coincides with the results of the paper [6] accomplished using too the SiO₂ + Al system with pre-activated quartz. To stabilize combustion at higher temperatures up to 20 % Al₂O₃ were entered in the sample as a ballast. The effect of pre-activation is enhanced by joint milling of SiO₂ and Al₂O₃ resulting in the decrease of more complete Si reduction temperature, at the same time the entered Al amounts being reduced (Table 1).

**Table 1**

| Charge composition           | T furnace, ℃ | SiO₂, % | Al₂O₃, % | 3Al₂O₃+2SiO₂, % | X-ray amorph phase, % | Si, % |
|-----------------------------|--------------|---------|----------|----------------|----------------------|------|
| Inactivated SiO₂ + 37.5 % Al | 670          | 37      | 12       | 7              | 31                   | 13   |
| Activated in centrifuge mill SiO₂ + 37.5 % Al | 630          | 37      | 12       | 5              | 35                   | 15   |
| Activated in planetary mill SiO₂ + 37.5 % Al | 570          | 33      | 18       | 19             | 13                   | 17   |
| Activated in centrifuge mill SiO₂ + 37.5 % Al | 850          | 19      | 27       | 20             | 19                   |      |
| Activated in planetary mill SiO₂ + 37.5 % Al | 850          | 10      | 15       | 12             | 28                   | 24   |
| Activated in planetary mill SiO₂ + 37.5 % Al | 1000         | 5       | 19       | 10             | 30                   | 35   |
| Activated in planetary mill SiO₂+ 37.5%Al + 20 % Al₂O₃ | 700          | 15      | 25       | 19             | 24                   | 17   |
Depending on the activation period the combustion temperature \( t_{\text{comb}} \) of activated quartz with aluminum of stoichiometric composition was determined using the pyrometer. The measurement results (Fig. 4) showed that in case of powder processing in the centrifuge and planetary-centrifuge mills these dependencies are in principle different ones. The synthesis was carried out in the furnace at 850 and 900°C temperatures. After processing in the centrifuge mill the combustion temperatures were lower than for non-activated quartz and after processing in the planetary mill the above mentioned values were higher ones. In first case they decrease and in second case they increase with activation time, respectively. Therefore, it may be expected that more complete silicon reduction from the quartz will be achieved in case of quartz processing in planetary mill (Table 1). In case of joint processing of quartz and aluminum in the planetary mill the combustion temperature is even more increased but in this case the dependence on the activation time is inverse one.

In case of alcohols introduction into the powder be activated the material conditions in result of its processing are substantially modified that is showed in the development of further combustion of the quartz with aluminum. For the quartz processed in the centrifuge mill with ethyl alcohol the temperature of combustion with aluminum at 850°C is higher that the temperature for material obtained by dry grinding. The maximum temperature is determined for the quartz mechanically processed during 10 minutes period. With activation time the \( T_{\text{comb}} \) decreases practically by exponent (Fig. 5). The similar dependence is observed for the quartz activated in presence of butyl alcohol but in this case the combustion temperature is substantially lower one. In case of furnace heating up to 900°C the combustion temperature increases for all samples. For the quartz of dry milling the regularities of temperature variations with activation time are remained the same ones, i.e. \( T_{\text{comb}} \) decreases with milling time. On the contrary, for the quartz activated in presence of alcohols \( T_{\text{comb}} \) increases with activation time. The quartz activated with butyl alcohol at 900°C temperature has the highest combustion temperature.

As above showed, the conditions of quartz activated in the planetary mill assure substantial combustion temperature increase. The processing in presence of alcohols in the mill of impact type as well as in the centrifuge mill of abrasion action modifies particle conditions in the manner that at 850°C the combustion temperature of aluminum with quartz activated in the ethyl alcohol increases and in contrast to the butyl alcohol this value decreases compared with SiO\(_2\) milled by dry method (Fig. 6). At 900°C the combustion process of quartz activated with butyl alcohol intensifies. In contrast to the centrifuge mill the dependence on the processing time in the planetary-centrifuge mill shows more complex characteristics.
mechanical quartz pre-processing with alcohols in the planetary mill during 10 - 15 minutes, as referred on the combustion temperature is substantially affecting on the process of solid phase synthesis. Longer exposure time results in decreasing of combustion temperature of system (SiO₂ + Al). The joint milling of quartz with aluminum in presence of ethyl alcohol during 5 - 10 minutes substantially increases the combustion temperature compared with the dry milled quartz. However, the prolonged processing, the lower process power characteristics. The use of butyl alcohol in process of milling of quartz with aluminum increases combustion temperature of activated mixture by 200 - 250°C. The time duration of quartz milling firstly results in changes of quartz particle dispersion degree. The dependence of thermodynamic characteristics of combustion reaction on the dispersion degree of mixture components is one of the most known and thoroughly studied for divers SHS systems. However, as our measurements showed, the quartz dispersion degree changes no monotonously depending on the time duration of its grinding in mills. The sizes of source quartz particles are up to ~ 200 µm. The quartz milling in the centrifuge mill (i.e., with predominant shift deformation action) during up to 15 minutes results in intensive grinding of quartz particles and their mean size decreases down to 5-10 µm. After quartz milling during 20 minutes there is occurred particle coarsening in average up to 50 µm, i.e., the coagulation process is running. However after 30 minutes milling the quartz dispersion degree is again increasing. The major part of powder particles has 10-15 µm size. A further increase of milling time duration up to 40 minutes results in coarsening of major mass of quartz powder up to 200-230 µm. The quartz milling during 60-80 minutes results in obtaining of mean particle size decreasing down to 80 µm. However, after quartz activation during 100 minutes the powder dispersion degree is again worsening and achieves up to 200 µm. Thus, from the above mentioned results of particle size measurement depending on the processing (milling) time duration there is evident that this process is running by stages, especially, the stage of intensive destruction is substituted by stage of particle coagulation. In case of quartz processing in the planetary-centrifuge mills with predominant mechanical impact action the grinding process is running similarly while the grinding degree being higher. The quartz milling during 10-15 minutes results in quartz grain size non-exceeding 5 µm. The further prolonged quartz milling up to 20-100 minutes results in changing of mean particle size.
within 100-150 \( \mu \text{m} \).

It should be noted that the coarse particles subjected to a prolonged grinding in the mill present quite sharp grains having shape rather of separate grains than of a conglomerate of stuck together small particles. Hence, the prolonged quartz grinding the destruction processes are running in association with intensive diffusion processes making available the efficient inter-growth of smaller particles into more coarse ones.

The quartz dispersion process is running somewhat unlikely with organic additions. The additions of up to 10\% of ethanol, butanol and polystyrene to the quartz be ground intensify the dispersion process. The quartz grinding during 15 minutes results in obtaining of mean particle sizes non-exceeding 5 \( \mu \text{m} \). The quartz grinding during more prolonged time period over 20 minutes results in obtaining of mean particle sizes from 10 to 80 \( \mu \text{m} \) with insignificant size variations depending on the processing time duration. Moreover there is observed a quite large-scaled scattering of particle sizes. At the same time in general quartz particle mass there are available both small particles (5-10 \( \mu \text{m} \)) and quite large ones (50-150 \( \mu \text{m} \)). The more coarse quartz particles processed with organic additions show irregular shapes, blurred boundaries. There is obvious that is resulted of smaller particle sticking into larger conglomerates. It should be noted that the type of organic additions practically affects no particle dispersion degree.

The above mentioned obtained dependence of combustion temperatures of SiO\(_2\)+Al system evidences that the role of dispersion degree in combustion process is apparent but it isn’t absolute one: the combustion temperature of the system after its processing in the planetary mill is higher. While the monotony (stages) is apparent by none ways of affecting the particle size variations. The conditions of activated surfaces and particle volumes of processed powder, especially in presence of organic additions, are exerting substantially more important effects.

The alcohol additions in process of quartz and quartz with aluminum milling serve both as surface active substances enhancing particle dispersion and result in more substantial modifications of the structure and power conditions of the material that is shown during further development of silicon oxide and aluminum interaction process.

It is known [1, 7] that the quartz is substantially amorphed in milling process. Moreover, on the particle surfaces in the amorphed layer there are formed active paramagnetic centers 'Si \( \equiv \) and 'SiO \( \equiv \) which interacting with gas media are transformed in long-living radicals. The reactive formations 'SiO \( \equiv \), enhancing particle dispersion result in more substantial modifications of material structure and its power conditions that is shown in further development of silicon oxide and aluminum interaction process. The reaction formation 'SiO \( \equiv \), named E' centers, the most actively interact with hydrocarbons. Besides of free radicals on the surface of milled quartz there are formed numerous non-paramagnetic centers of chemisorption. In result of interaction of these centers with atmospheric phase as well as with hydrocarbons on the particle surfaces depending on the processing environment media there may be formed divers compounds. For example, it is known [7] that the milling in the butanol results in the formation of polymer layers. The ethyl alcohol forms no chemical compounds, there is occurred only its physical adsorption on the particle surfaces. The surface polymerization of milled quartz is occurred more intensively in presence of more complex hydrocarbons, for example, polystyrene [7]. The above literature were using a base for generalization of these investigation results.

**Conclusion**

Dry quartz grinding in the mills-activators acting both mainly for abrasion effects with prevalent particle shifting deformation and for impact effects with prevalent compression deformation, enhances its power reserves which is realized in its further interactions with aluminum. In result of mechanical activation the temperature of mixture self-ignition in the furnace is decreased and the process of silicon reduction is runned out more completely. The milling with particle compression deformation assures higher power reserves, which is realized in process of quartz combustion with aluminum assuring higher temperatures in the combustion wave. The more processing duration, the higher degree of particle deformation and the more is its accumulated power. The prolonged grinding by abrasion (milling) on the contrary decreases combustion temperature. The X-ray structure analysis and EPR spectroscopy showed in this case a very expressed amorphization and formation of active deformation centers resulted of bond breakage those most part is subjected to recombinations interacting with atmospheric gases already in the milling process.

The additions of ethyl and butyl alcohols in the
quartz be dispersed result in first case in the intensive physical adsorption and in second case - in the chemisorption. The desorption of ethyl alcohol from the quartz surface increases temperature and speeds-up combustion process both at 850°C temperature and at 900°C. The formation of compounds by butanol on the quartz surface is already evidenced by the fact that it effects in different manner on the combustion process at above mentioned furnace temperatures. At 850°C and lower the combustion temperature of quartz decreases and at 900°C and over it increases. In first case obviously a part of heat is spent on the decomposition of organic quartz compounds; in second case the products of such compounds decomposition already in their turn participate in the redox reactions SiO₂ + Al intensifying this process.

These regularities are obtained for the quartz activated with modifying hydrocarbon additions in the both mills. Sole difference consists only in the fact that after processing in the planetary mill (with force compression effects) the effects of the modifiers on the temperature and completeness of redox reactions is showed more intensively. The availability of clearly expressed extreme point in the time dependence of the manifestation of activated material state proves the periodicity (alternation) of surface layer structure formation of quartz particles, including the formation of organo-metallic compounds with silicon on the broken bounds O - Si - O.

The use of more complex organic compounds as modifying additions: glycerine and polystyrene proves the above mentioned conclusion. These hydrocarbons are more active in the interactions with dispersed quartz and modify its surface structure in the manner that the mixture combustion temperature (SiO₂ + Al) of stoichiometric composition is decreased because a heat part is spent on the decomposition of surface modifying compounds. In this case the reaction are running-out more completely and practically with complete silicon reduction (Table 2).

### Table 2

Combustion temperature and phase composition of synthesis products obtained at 850 °C of Al and SiO₂ activated during 15 minutes with divers hydrocarbon modifications

| Hydrocarbon addition | Combustion temperature, °C | SiO₂, % | Al₂O₃, % | 3Al₂O₃+2SiO₂, % | X-ray amorph phase, % | Si, % |
|----------------------|-----------------------------|--------|----------|-----------------|----------------------|------|
| Ethyl alcohol        | 1650                        | 0.8    | 29.0     | 10              | 25                   | 23   |
| Butyl alcohol        | 1400                        | 1.5    | 27       | 2               | 15                   | 26   |
| Glycerine            | 1600                        | 2.0    | 34       | 2               | 10                   | 35   |
| Polystyrene          | 1350                        | 4.0    | 32       | 10              | 17                   | 40   |

The most striking effect was obtained in the mechanical mixture processing (SiO₂ + 37.5 % Al) with alcohols. In the joint milling of solid quartz and soft aluminum, the latter may be quite easily applied on the surface of solid particles. But this process isn’t a simple “physical spreading” of aluminum all over the quartz surface, firstly because a higher activity of the former and secondly, because a formation in milling process of reaction centers on the quartz surface. In the paper [1] it is showed, that in the milling process in the planetary mill there is occurred practically complete reduction of divers aluminum oxides. In milling process in presence of hydrocarbons it is naturally enough to expect that the organic compounds formed on the surface of quartz particle contain some aluminum. The investigations currently carried out on the structure of mechanically processed quartz prove this conclusion. The results of surface layer structure analysis of quartz particles modified by hydrocarbon compounds with aluminum or without it should be the object of our further reports.

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