

## SHS of Oxide Systems Based on MCR of 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  $\text{SiO}_2 + 37.5\% \text{ Al}$  system were investigated. The power saturation 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-ignited in the furnace, combustion temperature and completeness of the quartz reaction with aluminium were determined. The enhancing effects of organic modifiers of quartz particle surfaces on the further SHS synthesis development were shown.

**Key Words** : MCR(Mechano-Chemical Reaction), SHS, self-ignition, quartz reaction, combustion

### 1. Introduction<sup>1</sup>

The dispersion process of the quartz in the mills results in its profound micro-structure and morphology modification. 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 in a particle volume, and 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 mixture containing with both inorganic and organic compounds, the pressure is achieving up to  $10^9$  Pa in the contact points of divers material particles. It results in the diffusion rates being increased by few orders of magnitude and surfaces of 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 encapsulating them in the shell of new compounds. A quite

prolonged processing may cause the particle welding (sintering) of two divers materials and formation of a new compound [2]. It was known [3] that the thermodynamics and kinetics of redox reactions are depending on the powder dispersion degree. 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 was also known 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 reaction with powders result in formation of thin layers of organic and organo-metallic compounds on the solid particle surfaces. In process of further heating such organic formations are enable to be decomposed with formation of active radicals which may exercise a certain effects on the redox reactions running-out of inorganic material mixtures.

### 2. Experimental

The comparison of dilatometry measure results, i.e. variations of sample sizes with

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temperature  $\Delta L/L=f(T^{\circ}C)$  before and after mechanical material activation enables to estimate the degree of powder mixture activation. SHS synthesis was carried out with the  $SiO_2+Al$  sample having stoichiometrical composition. The quartz and its mixtures with aluminum were subjected to the mechanical activation in two mills, centrifuge and planetary-centrifuge 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 thermographical method, should not be equal values that is confirmed by dilatometry curves.

### 3. Results and discussion

The dilatometry curves of the quartz show a particular characteristics and consist of three sections with divers coefficients of linear of thermal dilatation (LTDC). 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 12 min., 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 min. and more in comparison with the samples in their initial and burned states (Fig. 1).

The quartz mechanically processed during 13

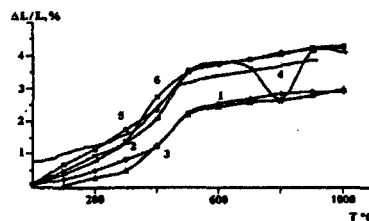


Fig. 1. Quartz dilatometry curves in its initial state and state activated in the centrifuge mill: 1-quartz in its initial state. The time to mill of quartz: 5(2); 10(3); 15(4); 20(5); 30(6) min.

to 18 min. is of particular interest. For it the section of dilatometry curve over  $500^{\circ}C$  shows the alternation (periodicity) of dilatation variations  $\leftrightarrow$  compression, i.e. the path of this curve section is not monotonic. After quartz milling during 3 min. and more in the planetary-centrifuge mill, there is occurred only the decrease of intensity and thermal dilatation degree (Fig. 2).

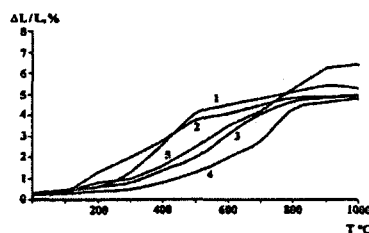


Fig. 2. Dilatometry curves of quartz activated in the planetary-centrifuge mill: 1-quartz in initial state and activated quartz: 2-10 min; 3-15 min; 4-20 min; 5-30 min.

In Fig. 3, it was presented the dependence of LTDC values ( $\alpha$ ) on the activation periods ( $\tau_{act}$ ) for three temperature ranges of sample heating ( $\alpha$ -quartz.  $\alpha \rightarrow \beta$  transition pre-conditions and  $\beta$ -quartz). The mechanical pre-activation is showed in the most degree at the stage of  $\alpha \rightarrow \beta$  transition pre-conditions. Depending on the activation period the LTDC within  $400-500^{\circ}C$  range varies by over one order of magnitude both in direction to the decrease and 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. The structure modifications of quartz particles during 20 min. were sharply reduced their thermal dilatation and the further dispersion process only enhancing the thermal dilatation intensity increasing. For material processed in the planetary-centrifuge mill, on the curves  $\alpha = f(\tau_{act})$  there is observed only sole extreme point which falls on the 20 min. period of activation. After particle pre-activation conforming both to the thermo-graphical and dilatometry analysis data the temperature of  $\alpha \rightarrow \beta$  transition and such variations occurred within 90-150°C range depending on the exposure time and showed non-linear characteristics.

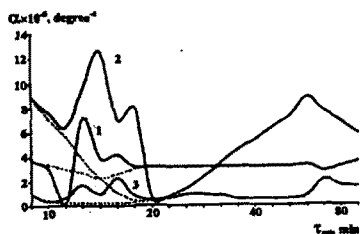


Fig. 3. Dependence of linear thermal quartz dilatation-coefficient on pre-activation time.

In the centrifuge mill the  $\text{SiO}_2$  particles in more significant manner were subjected to shifting deformation (milling) and in the planetary-centrifuge mill to the compression (impact). In first case there was occurred a more intensive grinding and amorphization of particle surfaces layers, and in second case the more intensive volume modifications of particle structure were occurred. The amorphization of quartz particle surfaces was occurred in the both cases, but as it was proved by X-ray structure analysis in the centrifuge mill the amorphization was more intensive. It may be expected that the differences or the structure modifications of

particle surfaces and their volumes depending on the exposure period in the mills with divers schemes of force effects would contribute their particularities in the development of SHS synthesis of activated quartz. The examined regularities were proper for the quartz namely. The activated iron and aluminum oxides showed only LTDC increase with the activation period in the both mills. SHS synthesis was carried out using the pre-activated quartz and its mixtures with aluminium of stoichiometric composition. The effects of activation duration on the self-ignition, combustion temperature and reaction completeness were determined by phase compositions of synthesis products at divers temperatures of furnace heating (Table 1).

Table 1. Phase composition of synthesis products

Charge composition	T °C furnace	$\text{SiO}_2$ , %	$\text{Al}_2\text{O}_3$ , %	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , %	X-ray amorph. phase, %	Si, %
Inactivated $\text{SiO}_2 + 37.5\% \text{ Al}$	670	37	12	7	31	13
Activated in centrifuge mill $\text{SiO}_2 + 37.5\% \text{ Al}$	630	37	12	5	35	15
Activated in planetary mill $\text{SiO}_2 + 37.5\% \text{ Al}$	570	33	18	19	13	17
Activated in centrifuge mill $\text{SiO}_2 + 37.5\% \text{ Al}$	850	19	27		20	19
Activated in planetary mill $\text{SiO}_2 + 37.5\% \text{ Al}$	850	10	15	12	28	24
Activated in planetary mill $\text{SiO}_2 + 37.5\% \text{ Al}$	1000	5	19	10	30	35
Activated in planetary mill $\text{SiO}_2 + 37.5\% \text{ Al} + 20\% \text{ Al}_2\text{O}_3$	700	15	25	19	24	17

After  $\text{SiO}_2$  activation in the centrifuge and planetary-centrifuge mills the furnace temperature assuring the sample self-ignition was 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 resulted in the alteration of the combustion stability. It was running conforming

to the thermal explosion type. It coincides with results of paper [4] accomplished using  $\text{SiO}_2+\text{Al}$  system with pre-activated quartz too.

To stabilize combustion at higher temperatures up to 20 %  $\text{Al}_2\text{O}_3$  were entered in the decrease of more complete Si reduction temperature, at the same time the entered Al amounts being reduced (Table 1).

#### 4. Conclusion

In result of mechanical activations the temperature of mixture self-ignition in the furnace was decreased and the process of silicon reduction was run out more completely. The X-ray structure analysis and EPR spectroscopy showed in this case a very expressed amorphization and formation of active deformation centers. 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 chemical adsorption. The desorption of ethyl alcohol from the quartz surface increases temperature and speeds-up combustion process both at 850°C and 900°C. The formation of compounds by butanol on the quartz surface was already evidenced by the fact that it effects in different manner on the combustion process of above mentioned at furnace temperatures. At the 850°C or lower, the combustion temperature of quartz was decreased, and at 900°C or over, it was increased. In first case obviously a part of heat was spent on the decomposition of organic quartz compounds, but in second case the products of such compounds decomposition already in their turn participate in the redox reactions  $\text{SiO}_2+\text{Al}$  intensifying this process. These regularities were obtained for the quartz activated with modifying hydrocarbon additions in the both mills.

The use of more complex organic compounds as modifying additions, glycerine and polystyrene proved the above mentioned conclusion. These hydrocarbons were more active in the interactions with dispersed quartz and modified its surface structure in the manner that the mixture combustion temperature ( $\text{SiO}_2+\text{Al}$ ) of stoichio-

metric composition was decreased, because a heat part was spent on the decomposition of surface modifying compounds. In this case the reaction were running-out more completely and practically with complete silicon reduction.

The most striking effect was obtained in the mechanical mixture processing ( $\text{SiO}_2+37.5\%$  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 is not a simple "physical spreading" of aluminium 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 milling process in presence of hydrocarbons it is naturally enough to expect that the organic compounds formed on the surface of quartz particle containing aluminum. The investigations currently carried out on the structure of mechanically processed quartz proved 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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