Features of Combustion in Mechanically Activated SiO_2–Al System

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Abstract

The effect of mechanical activation of quartz (separate and joint with aluminium) and abrasion-reaction wear of the material of milling bodies on the induction period and temperature of thermite process of obtaining sintered materials based on quartz is investigated.

INTRODUCTION

The nascent growth of industrial and civil construction requires not only new materials with a broad range of physicochemical properties but also highly efficient technologies of their production. First of all, this relates to the synthesis of ceramic hardware; the traditional technology of their production is characterized by special requirements to the initial raw material resources and high energy consumption per product unit. Because of this, it becomes urgent to solve the problems connected with intensification of separate technological processes and the production in general, especially mixture preparation and thermochemical processes with the participation of the solid phase.

One of the promising routes to solve this problem is the synthesis of materials in the regime of solid-phase combustion or self-propagating high-temperature synthesis (SHS) [1, 2], which has become a real technological operation for obtaining entire classes of inorganic compounds. Unlike the traditional sintering processes, SHS proceeds within relatively short time intervals, require much less energy consumption, are distinguished by almost complete absence of production wastes. In the technological aspect, the synthesis of new materials in the SHS regime does not require complicated engineering solutions. From the practical point of view, when obtaining various products for construction, mix SHS systems containing silicon dioxide (SiO_2) are specially preferred, because this material comprises the basis of the major part of natural minerals and wastes of construction industry.

Previously we demonstrated the possibility to use SHS method in the technology of obtaining multifunctional ceramic tiles which allowed substantial decrease in the time of thermal treatment and at the same time to reduce temperature [3–5]. The regularities of formation of high-strength structures in the systems based on silicon dioxide were considered therein. However, calculations did not indicate sufficient economical efficiency of the proposed technological solutions due to relatively high concentration of an energy carrier in the initial reagent mixture and its price in the home and foreign markets. In order to increase economical attractiveness of SHS application, it is necessary to search for reasonable ways to further improvement of the technological operations of raw material preparation and roasting processes.

One of the factors affecting solid-phase agglomeration and combustion is change in the reactivity under the action of mechanical activation (MA). A numerous group of research works was dedicated to the investigation of MA. For practical purposes, it seems interesting to obtain the materials with increased reactivity at the preliminary stage of material preparation due to the accumulated mechanical energy which would be realized in subsequent technological operations.

In the present work we consider the behaviour of silicon dioxide under the action of MA in mills of different kinds with steel milling tool accessories during agglomeration and aluminothermic combustion. Such a choice of the subject of investigation is due to high abrasive ability of quartz particles and also due to the known data on the possibility of milling tool material to participate in mechanochemical reactions [6, 7].

EXPERIMENTAL

Investigation was carried out with quartz samples (rock crystal, 99.8 % purity with respect to SiO_2). MA was carried out with a ball mill (BM) and a three-cylinder planetary centrifugal mill (PCM) described in [8]. The degree of particle size reduction (grinding) of the samples was determined by means of thermal desorption of argon with addition disaggregation [9]. In order to determine possible forms of the presence of iron in quartz particles, the activated material was subjected to acid etching according to the procedure described in [10], then the samples were investigated using the traditional methods of analysis (electron microscopy, XPA, NGRS, IR spectroscopy). Sample preparation for investigation of combustion processes was carried out using a procedure described in [11]. Temperature in the profile of combustion wave was recorded with a loop oscillograph using a tungsten-rhenium thermocouple which is distinguished by high sensitivity within the temperature range under investigation.

RESULTS AND DISCUSSION

The data on the changes of specific surface and mass concentration of iron originated from abrasive wearing of the milling bodies *versus*

TABLE 1

Specific surface and mass concentration of iron in quartz samples depending on MA time τ

Mill type	Time of MA τ, min	Specific surface $S(\tau)$, m^2/g	Mass concentration of iron, %		
			Gravimetric method	After etching	
				Spectrography	Microprobe
PCM	0	(~ 0.01)	(0.06)	–	–
	5	1.1/1*	1.43	0.10	–
	10	4.6/5.3*	2.68	0.18	0.16
	15	2.7/6.8*	3.74	0.24	0.23
	30	2.7/7.2*	3.90	0.41	0.35
	60	2.7/7.2*	4.50	0.52	–
	90	2.7/7.2*	5.14	0.64	0.40
BM	120	0.2/ –	–	–	–
	180	0.5/ –	–	–	–
	300	1.01/ –	–	–	–

* Specific surface after disaggregation.

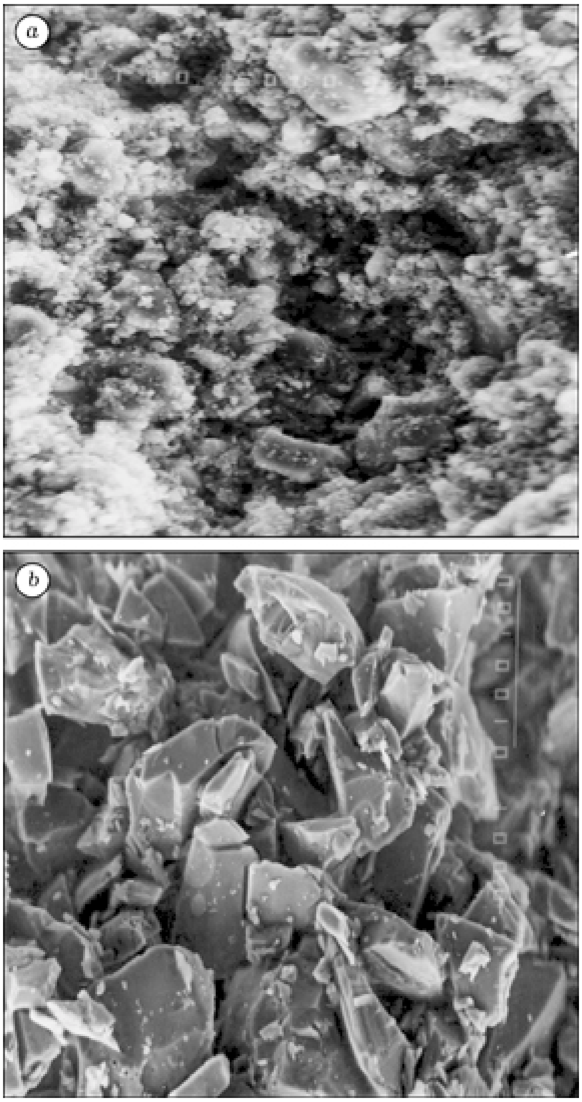

Fig. 1. Electron microscopic images of agglomerated samples after MA of quartz in planetary centrifugal (*a*) and ball (*b*) mills.

time of mechanical activation τ are shown in Table 1.

It is known that the activity of quartz in physical and chemical processes depends not only on the disperse state of the material but also on its structural and energy state [12]. This may be confirmed by the data on agglomeration of quartz samples with iron washed away, characterized by identical specific surface but subjected to MA in the mills of different types (Fig. 1, Table 1). In the electron microscopic images, one can clearly see the differences in the behaviour of the material after thermal treatment. For quartz samples activated mechanically in a PCM, the particles are fused and connected with each other through the amorphous phase. The structure of samples after MA in a BM is represented by separate fragments. A similar dependence may be observed also with the amount of quartz that passes into the tridymite-cristobalite phase at the roasting temperature (1300 °C) (Table 2). Such a behaviour of the material is explained according to [12, 13] only by an increase in the amount of defects in the structure and by changes in the energy state of the surface layers of quartz activated mechanically in a PCM.

At the same time, basing on the size of iron particles originating from the abrasive wearing of steel milling bodies of the PCM, the formation of iron silicates on the surface of quartz during MA was proved theoretically and experimentally by us [8, 9, 14].

The data on the form in which iron is present were obtained by means of NGRS and IR spectroscopy (Fig. 2). It follows from the data of NGRS that additional lines are observed in the spectra of the samples (see Fig. 2, *a*) after MA in PCM. These additional lines provide evidence of changes in the character of iron atom bonding with the surroundings. The internal part of the spectrum is described by the quadrupole doublet with hyperfine splitting

TABLE 2

The degree of polymorphous transformations of quartz activated mechanically in a ball and planetary centrifugal mills

Mill type	MA time, min	Roasting time, h	Phase composition, mass %	
			Quartz	Tridimide + Cristobalite
PCM	15	60	48	52
»	15	120	35	65
»	15	180	30	70
BM	100	60	85	15
»	100	120	67	33
»	100	180	55	45

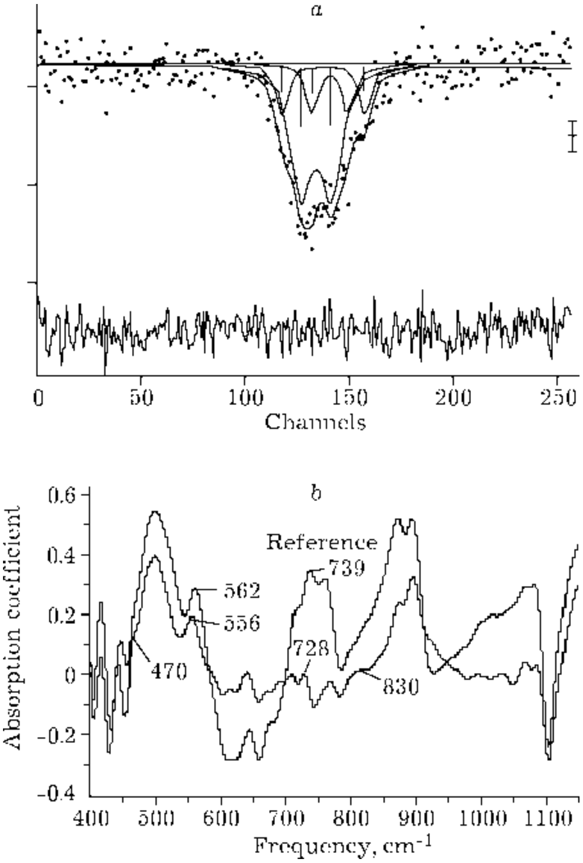

Fig. 2. Spectroscopy of MA quartz: *a* – nuclear gamma resonance spectroscopy, MA time: 90 min; *b* – infrared spectroscopy, MA time: 10 min.

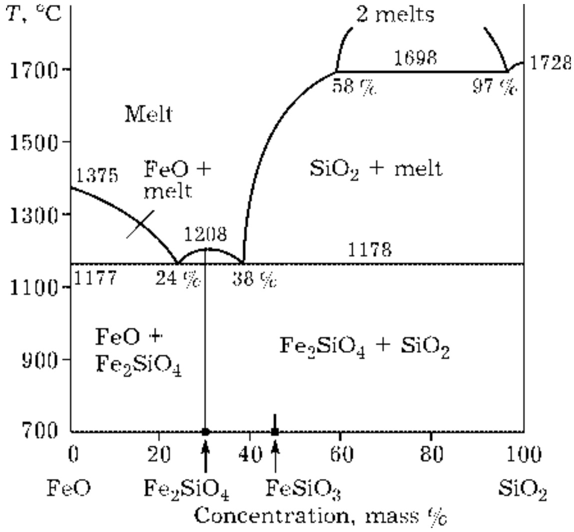

Fig. 3. Diagram of state for FeO–SiO$_2$ system [21].

constants pointing to the fact that iron occupies two non-equivalent positions in the quartz lattice. According to [15, 16], such a feature of iron ions on the quartz surface can be explained only by the formation of iron silicates. The formation of iron silicates is indirectly confirmed by the IR spectroscopic data for the initial and mechanically activated quartz samples (see Fig. 2, *b*). No differences in the bands related to Si–O–Si and O–Si–O bonds were detected in the samples under comparison. However, a band at ~833 cm^{-1} appears in the activated sample; it is assigned to Si–O–Me bond [17]; the absorption band related to Si–OH bond (~881 cm^{-1}) disappears.

When obtaining silica refractory bricks, mineralizer additives are used to reduce temperature (1470 °C) and time of phase transition SiO$_2$ (quartz) → SiO$_2$ (cristobalite) [18–20]. In this case, iron silicates formed on the surface of quartz particles during MA can also serve as mineralizers because their melting point is much lower (~1200 °C) (Fig. 3) [21]. During calcination of mechanically activated quartz, iron silicates act as a lower-melting admixture and increase the amount of the liquid phase; its viscosity drops with an increase in temperature [20]. This promotes more complete agglomeration of mechanically activated samples and increase in the degree of polymorphous transformations in the systems based on silicon dioxide [13].

The phenomena observed during MA of silicon dioxide in a PCM affect not only agglomeration processes but also the kinetic parameters, reaction mechanism, composition and structure of the final products in SHS type reactions. Investigations of the combustion of mechanically activated component mixtures in SiO$_2$–Al system were described in [11, 22]; a decrease in the starting synthesis temperature and an increase in the kinetic parameters of combustion were described for mechanically activated samples in comparison with non-activated ones. The authors of those works explain this fact both by an increase in defect content of the crystal structure and by initiation of the interaction between reagents even before the start of exothermal reaction. At the same time, the authors of [11, 22] did not take into account the role of impurities introduced as a result of abrasive reaction wear of the steel milling tool accessories. Investigation of the effect of this factor on the technological combustion processes in the mixtures of quartz with aluminium subjected to mechanical

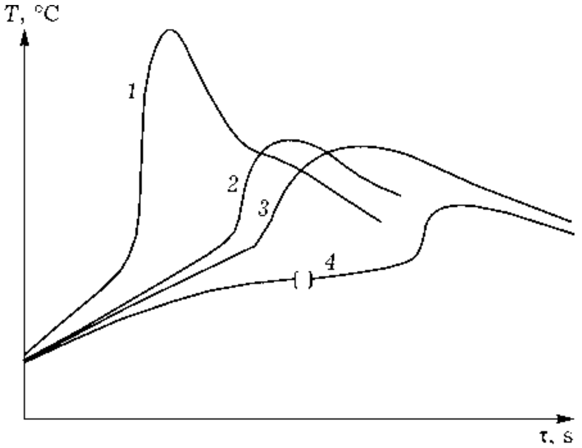

Fig. 4. Dependence of combustion wave profile on the time of preliminary MA: *1* – BM, 1400 °C; *2* – PCM, 1200 °C, 20 min; *3* – PCM, 30 min; *4* – PCM, 1070 °C, 90 min.

activation is of definite research and practical interest.

It follows from the experimental dependencies of temperature profiles of combustion wave (Fig. 4) that the temperature of the combustion wave front decreases with an increase in MA time. Broadening of the reaction zone is observed with mechanically activated quartz sample, which, in agreement with the concept of broad zones of reaction [23], corresponds to strong braking of the interaction between the components. Such a behaviour of silicon oxide samples mechanically activated in PCM exhibited in aluminothermic processes can also be connected with an increase in the amount of iron silicates (see Table 1), because they modify the surface of quartz particles and can serve as a diffusion barrier [24] preventing aluminium from penetrating to the quartz surface.

The performed experimental investigation showed that the intensity of MA affects also other macrokinetic characteristics, such as delay time of the start of synthesis, maximal temperature and rate of combustion (Table 3). It was established with the help of X-ray phase analysis of combustion products that the best silicon reduction in the aluminothermic reaction of quartz is observed for the samples activated in BM, and for the samples with the shortest time of activation in PCM (Table 4).

The combustion of mechanically activated silicon dioxide with aluminium was carried out according to the procedure described in [11] using a furnace heated to 800 °C under usual atmospheric conditions. At this temperature, melting of metal aluminium occurs [25], but iron silicates on the surface of quartz particles do not melt. In this case, diffusion of liquid aluminium to the surface of quartz particles occurs through a layer of iron silicates which can act as diffusion barrier increasing the

TABLE 3

Macrokinetic characteristics of combustion process in the system SiO_2 (63 %) + Al (37 %)

Mill type	MA time, min	Induction period of ignition, s	Ignition temperature, °C	Combustion time, s	Maximal combustion temperature, °C	Mass combustion rate, g/s
BM	300	3.30	900	20	1520	0.5
PCM	10	5.30	900	20	1220	0.5
»	30	6.20	950	40	1200	0.25
»	90	15.8	950	80	1000	0.12

TABLE 4

Composition of combustion products in the system SiO_2 (63 %) + Al (37 %), %

Mill type	MA time, min	SiO_2	Al	Si	Al_2O_3	$3Al_2O_3 \cdot 2SiO_2$	Amorphous phase
BM	300	7.7	8.0	24.4	31.3	13.9	14.7
PCM	10	22.2	9.6	18.3	27.5	12.1	10.3
»	30	31.3	13.4	11.8	30.8	8.6	4.1
»	90	40.5	15.4	7.0	33.9	2.2	3.2

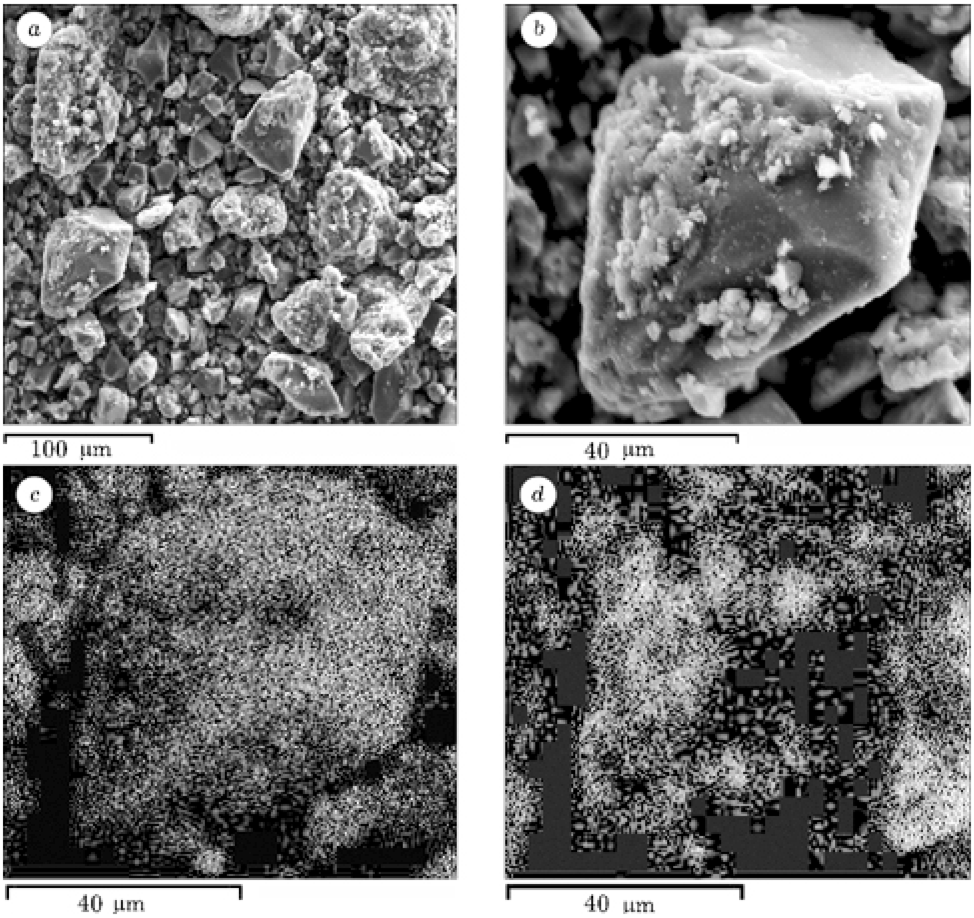

Fig. 5. Electron microscopic images of SiO_2 + Al mixture after MA: *a* – the general view of the mixture; *b* – agglomerate composed of SiO_2 and Al particles; *c*, d – the appearance of the agglomerate in the radiation of silicon and aluminium, respectively.

induction period of the reaction and causing partial loss of aluminium due to oxidation. Considering the combustion mechanism in the indicated system, we focused only on the concept of broad reaction zones and quite admitted the occurrence of mechanisms connected also with diverse changes in the dynamics of heat evolution in mechanically activated thermite mixtures [11, 22].

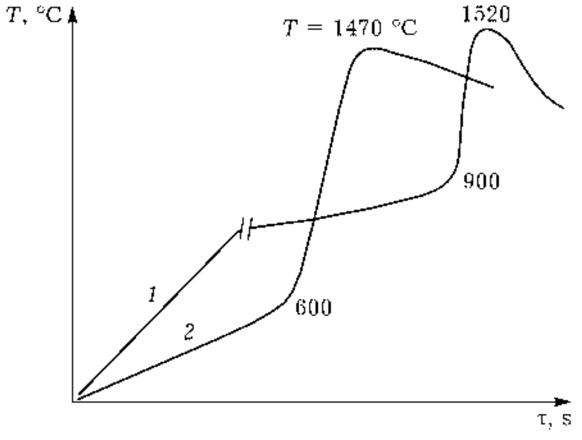

Fig. 6. The effect of the joint MA of SiO_2 and Al on combustion of the mixture: *1* – BM, *2* – PCM.

In order to prevent the formation of iron silicates at the stage of MA of quartz, we carried out the experiments on MA of thermite mixture if quartz with aluminium. Aluminium as a more plastic material, coats the surface of steel material of milling bodies preventing their wear and abrasive reaction modification of the surface of quartz particles (Fig. 5).

One can see in Fig. 5 that as early as after MA for 10 min the sharp faces of quartz particles become rounded; aluminium particles are observed to stick on their surface. The microprobe analysis of agglomerates indicated the absence of elemental iron in the reaction mixture.

Mechanical activation of SiO_2–Al system causes changes in the character of aluminothermic combustion of the mixture (Fig. 6). According to the obtained profiles of combustion wave, the induction period in the samples activated jointly in PCM is much shorter than that for the samples activated in BM, while temperature of the start of exothermal reaction shifts to lower values, which is connected with the removal of diffusion barriers due to the formation of Al–O–Si bond [22].

CONCLUSIONS

The investigation showed that MA of silicon dioxide in different mills affects the behaviour of the treated material in subsequent thermochemical and metallothermic processes. The samples of quartz after MA in a planetary centrifugal mill are prone to more intensive agglomeration in comparison with the samples mechanically activated in a ball mill. Such a behaviour of the material is connected not only with the changes in the defect state of crystal structure but also with abrasive reaction modification of the surface of quartz particles with iron silicates.

The layers of iron silicates can act as diffusion barriers in metallothermic processes; they prevent the direct contact between the components of reaction systems. The joint mechanical activation of quartz and aluminium prevents wear of the steel material of milling bodies and, as a consequence, the formation of iron silicates on the surface of mechanically activated quartz particles.

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