

Carbon as an Effective Modifier of Silicon Dioxide and Reagent for Obtaining Nanostructured SHS-Composites

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Abstract

The peculiarities of the structure and morphology of quartz particles modified by carbon depending on MCT conditions and type of specific carbonaceous modifier were studied. Powder materials with the composition structure of the materials, which are hybrid formations organics-inorganics with a high chemical activity of its components, were obtained by combined MCT of carbon or carbon containing organic compounds with quartz. A high chemical activity of quartz particles modified by carbon is effectively realized when producing SHS-ceramics composition materials. The rate of redox processes increases, the initial reagents are most completely realized and nanosized particles of silicon carbide are formed. It is shown how one can regulate the process of combustion in SH-synthesis and produce the material of the necessary quality by modifying silicon dioxide particles in the course of MCT.

Introduction

Researchers and technologists have paid an exclusively great attention to nanostructured systems, methods of their synthesis, study of their structure and properties, determination of the field of their most effective use lately. Different inorganic, organic and composition nanosystems are synthesized in both a disperse and compacted state which are of great importance in sorption, catalysis, electronics, production of sensor systems and other fields of engineering [1]. In any of these cases there is a subject of streamlined synthesis and investigation of surface nanostructures [2]. When obtaining such composition nanomaterials, special attention is paid to carbon- and silicon containing systems. Carbon and silicon dioxide occur in nature in abundance, have a great number of different polymorphous modifications, form both organic and inorganic compounds and are basic substances, when creating many materials in different technological processes including mechanochemical

treatment (MCT) and technological combustion – self propagating high temperature synthesis (SHS).

We have earlier shown [3-5] that MCT of quartz in the presence of organic additives-modifiers results in formation of surface nanostructured layers with the thickness of 10-50 nm encapsulating a quartz particle into shells of different composition. Carbon containing modifiers play a significant role in this process. The synthesized material is characterized by new sorption and electromagnetic properties, thereby determining its function as a magnetic sorbent [4].

This work deals with a wider range of carbon containing additives-modifiers with the aim to study in detail the regularities of formation of the structure and morphology of the surface layers of a quartz particle being dispersed and its activity in further chemical reactions of combustion under the conditions of SH-synthesis.

Experimental

Mechanochemical treatment of quartz in combination with different organic compounds (polyvinyl alcohol, succinic acid, acrylic acid,

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polystyrene, carbon), was carried out in a mill of a centrifugal-planetary type. The additives were introduced in the amount from 5%. Milling was performed with the rotation velocity of the platform 700 r/min. The rotation velocity of milling vessels made up 1200 r/min, acceleration reached 20 g. The time of MCT varied from 5 to 30 min.

The obtained material was studied by the methods of X-ray phase, X-ray structural, electron microscopic analyses. Density, specific surface and the amount of carbon in the modified specimen were measured using standardized methods. The sequence of structural rearrangement of surface carbon containing layers of quartz particles depending on the modifier and conditions of mechanochemical treatment was analyzed.

SHS was carried out by a furnace method under the conditions of self-ignition of the sample (SiO_2 - Al) of a stoichiometric composition placed into a preheated furnace. The temperature of furnace heating made up 900°C. The samples were moulded on the laboratory press "Carver" with the force of 10t with the sizes: diameter (d) = 20 mm, height (h) = 20 mm. The temperature of combustion was measured by a pyrometric thermometer Ircon Ultrimax Plus UX10P. The temperature, time of sample heating and procedure of the reaction itself were measured, and the rate of the reaction development was calculated. The completeness of the reaction was determined by the phase composition of synthesis products.

Results and Discussion

The electron microscopic investigations of quartz particles have shown that, when adding organic additives into the quartz being dispersed, the structure of particles undergoes significant changes. The surface layer is a multilayer formation of different morphology and density (Figure 1). The more complex is the used carbon containing modifier by its structure (in sequence – monoatomic and multiatomic alcohols, acids and polymers), the more various is the morphology of the modified surface layer of a quartz particle due to mechanochemical treatment. These changes are, first of all, due to the nature of the modifying additive. The increase in the amount of carbon in the modifier results in formation of a dense, quite homogeneous organic film on the surface of a quartz particle. Besides, when using succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) and acrylic acid ($\text{C}_3\text{H}_4\text{O}_2$), nanosize carbon containing round and film formations are observed on the surface (Figure 1 b, c). At MCT in the presence of polyvinyl alcohol [$\text{C}_2\text{H}_3\text{OH}$] n and polystyrene [C_8H_8] n , a denser film is formed on the surface of particles (Figure 1d). When using polystyrene, also, formation of carbon tubes of a complex configuration was observed on the modified surface (Figure 1 e). According to the results of electron diffraction, a distinguishing peculiarity of such formations is texturization, i.e. preferential orientation.

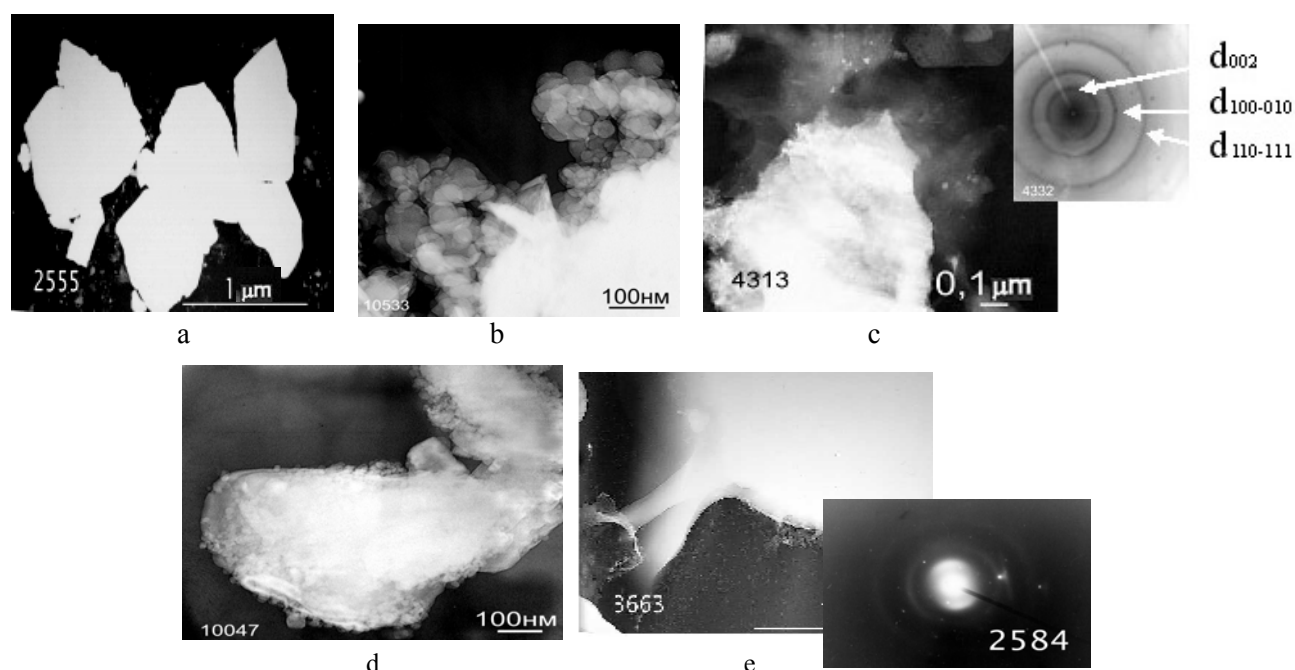


Fig. 1. Electron microscopy and diffraction of the surface of quartz particles in the initial state (a) and modified by succinic acid (b), acrylic acid (c), polyvinyl alcohol (d) and polystyrene (e) in the process of MCT

In this case the amount of carbon in the modified surface layer of quartz reaches 3% and the specific surface of quartz particles exceeds 46 m²/g compared to that obtained without a modifier – 5.2 m²/g. The specific surface and density of particles with modified surface are quite sensitive characteristics of the change in the structure and microstructure of the surface layer of particles treated in the presence of organic additives. Table 1

presents the results of measuring these characteristics for quartz subjected to mechanical treatment with different organic modifiers and, also for comparison, with carbon which, first of all, provides mechanical enveloping of particles being dispersed in its presence. For comparative evaluation, the time of mechanical treatment of (τ_{MCT}) = 20 minutes and the same amount of the introduced modifier (5%) were chosen.

Table 1

Specific surface (S_{sp}), apparent (ρ_{app}) and pycnometric (ρ_p) density, the content of carbon in the modified layer of quartz particles after of MCT.

Material	S_{sp} , m ² /g	Density ρ , g/cm ³		C, %
		(ρ_{ap})	(ρ_r)	
SiO ₂	5.20	2.55	2.65	-
SiO ₂ +5% AA*	56.6	0.82	0.94	2.03
SiO ₂ +5% SA**	52.7	0.87	0.97	1.78
SiO ₂ +5%PVA***	21.0	0.65	0.67	2.4
SiO ₂ + 5%PS****	46.7	0.58	0.62	3.0
SiO ₂ + 5%C	77.6	0.88	0.91	5.0

*AA – acrylic acid, **SA – succinic acid, ***PVA – polyvinyl alcohol, ****PS – polystyrene

When modifying by acids, the specific surface of particles increases by an order and reaches 52.7-56.6 m²/g in comparison with the particles treated in the mill and in the presence of activated carbon when the specific surface increases up to 77.6%. For quartz, a significant increase of specific surface after 20 minutes of treatment is related to the increase in the share of high disperse particles and loosening of the surface layer and due to the change in the structure of the surface layers of particles, i.e. their modification. Dispersity, structure and state of particle surface significantly influence the value of bulk density of the powder. Table 1 presents the values of pycnometric density compared to the data on the apparent density. The decrease in pycnometric density and the difference between the pycnometric and apparent density indicates the increase in porosity of the powder being analysed. The most significant changes of specific surface and density of quartz particles at treatment of quartz with 5% activated carbon can only take place in the case when not only enveloping of quartz by carbon occurs but also their active interaction with the change in the structure of the surface layer of particles.

Acrylic acid (H₂C=CH-COOH) is known [6, 7] as one of the most active modifiers of inorganic

materials. Even at a slight mechanical action (grinding in a mortar) acrylic acid and styrene polymerize. At intensive mechanical grinding polystyrene undergoes destruction and repolymerization [6, 8]. Therefore, acrylic acid and polystyrene were chosen as modifiers with an expressed ability to polymerization and destruction. Polyvinyl alcohol gets actively destructed to carbon and the use of succinic acid as a modifier results in both saturation of the surface with carbon and its hydration on active centers of the juvenile surface of dispersed quartz.

The results of X-ray structural analysis show that the presence of organic modifier leads the change of the defect structure in the volume of the particle, i.e. in a quartz particle. Organic formations on the particle surface are not registered by the X-ray structural method, in this case they are “transparent” for it. It is stated (Fig. 2) that the presence of modifiers, for example polystyrene, after 20 minutes of treatment evidently contributes to the decrease in the size of crystallites and the increase in widening of X-ray line [9], i.e. the increase of volume defectness of samples and, consequently, the change of its energy state. With further increase in the period of treatment the size of crystallites does not practically change but the

X-ray line continues to widen. Hence, using a modifying organic additive during MCT it is possible to significantly effect the change of the internal structure of the inorganic material being dispersed.

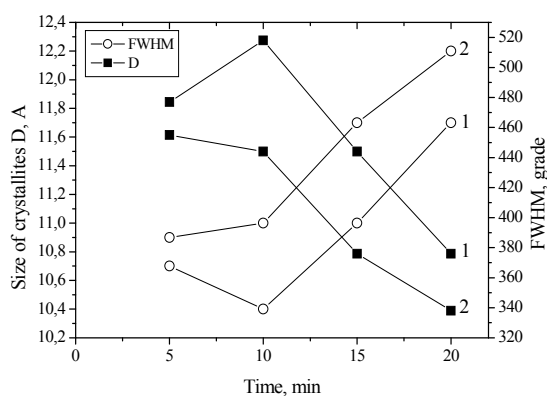


Fig. 2. The change in the width of X-ray line (FWHM) and the size of crystallites (D) depending on the time of treatment of quartz activated without (1) and in the presence of polystyrene (2)

The synthesized particles are proved to be microcomposition objects with a complex structure by the results of dilatometric investigations which at the same time indicate the change in the energy state of the material. Saturated with carbon polymer compounds being synthesized at MCT and modifying quartz get destructed in the process of heating which is clearly shown by the shape of dilatometric curves (Fig. 3). However, the peculiarities of the shape of dilatometric curves for the samples modified by acrylic acid and polystyrene, namely, the presence of plateau in the range before 150-200°C indicates the fact that there is forming not simple organic polymers but compounds with a complex structure which considerable reduce CLTE (coefficient of linear thermal expansion) of the material. The presence of organic additives and their burning out would intensify thermal widening of the sample. The observed run of the curves indicates modification of the structure of quartz particles, the presence of new carbon containing compounds on their surface.

Such quartz particles modified by carbon are characterized by a high chemical activity which is effectively realized when producing SHS-ceramic composition materials. After MCT of quartz, the induction period decreases and the rate and temperature of combustion increase. Fig. 4 presents thermograms of combustion of systems with quartz in the initial state and modified by succinic acid, polyvinyl alcohol and polystyrene. The more

carbon in the additive-modifier, the more intensive is the process of combustion and the more completely the initial reagents are realized. Maximum temperature of combustion reaches 1400°C and more.

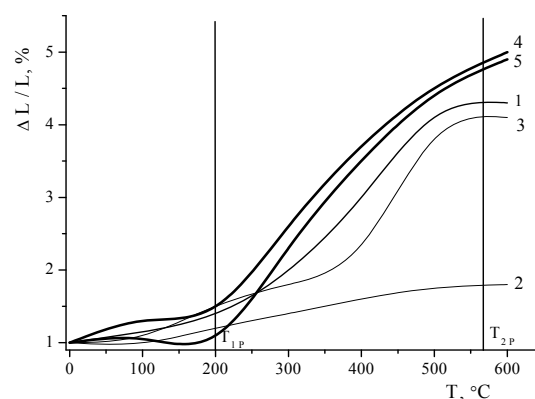


Fig. 3. Dilatometric curves of quartz, in the initial state (1), activated without modifiers (2) and in the presence of 5% of polyvinyl alcohol (3), acrylic acid (4) and polystyrene (5).

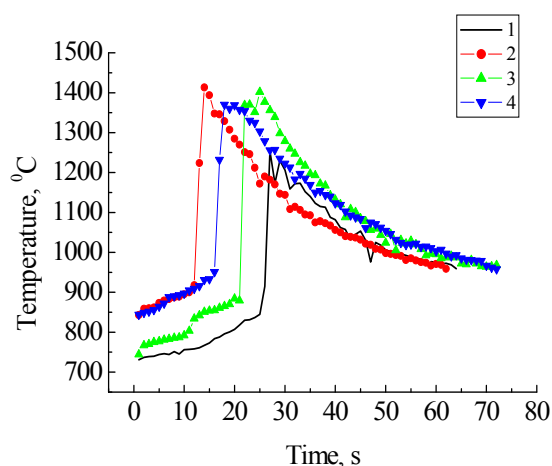


Fig. 4. Thermograms of combustion of $(\text{SiO}_2+37.5\%\text{Al})$ system with quartz in the initial state (1) and activated during 30 minutes in the presence of modifier: 2 - $[\text{C}_2\text{H}_3\text{OH}]_n$, 3 - $[\text{C}_8\text{H}_8]_n$, 4 - $(\text{C}_4\text{H}_6\text{O}_4)$.

The time of treatment plays a significant role in the development of the modifier effect on the combustion process and the change in maximum temperature of combustion. When using polystyrene as a modifier, maximum temperature of combustion (1570°C) is registered after 20 minutes of MCT of quartz (Fig. 5) and, when using acrylic for modification, maximum thermokinetic characteristics of the combustion process are stated after 15 minutes of MCT. The combustion temperature of quartz modified by succinic acid is much lower than when modified by polystyrene.

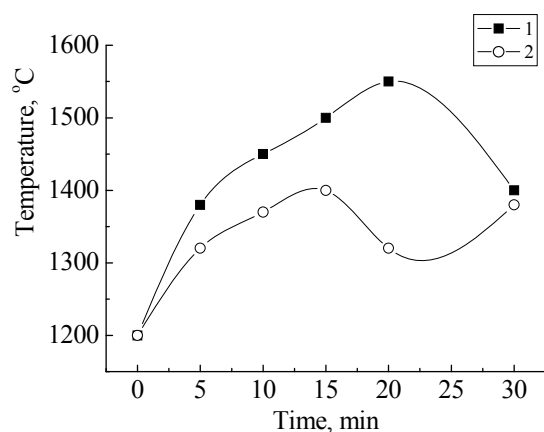


Fig.5. Dependence of maximum combustion temperature of the system (SiO_2+Al) of a stoichiometric composition on the time of mechanochemical activation: 1 - quartz + 5% of polystyrene, 2 - quartz + 5% of acrylic acid.

The combustion products contain nanosize particles of silicon carbide uniformly distributed in the volume of aluminium oxide. The amount of

synthesized silicon carbide reaches 10%, when using polystyrene as a modifier (Table 2). Quartz modified by acrylic acid and polyvinyl alcohol is most completely reduced to Si. Besides, in all SHS samples there is $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (mullite) and FeSi_2 . The latter compound is in an ultradisperse state too. The iron enters to the quartz powder because of rubbing the steel milling vessels and grinding balls from the surface during the process of mechanochemical treatment.

SHS-composite synthesized on the basis of quartz modified with carbon containing substances after MCT is distinguished by high strength. It the strength of samples obtained on quartz activated without modifiers changes within the range 20-25 MPa depending on the time of MCT, modification with acids (succinic and acrylic acids) provides the increase in the strength of SHS-samples up to 40 MPa and in case of modification with polyvinyl alcohol and polystyrene – up to 50 and 65 MPa, respectively.

Table 2

The phase composition of synthesis products at 900°C AL with SiO_2 activated during 20 minutes with and without modifiers

Modifiers	SiO_2 , %	Al_2O_3 , %	$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, %	Si, %	FeSi_2 , %	SiC, %	XAF*
	12	17	17	22	-	-	32
5 % SA**	2	35	8	32	5	3	15
5 % AA***	2,7	35	2,3	34	7,0	5	14
5% PVA****	4	30	6	33	5	7	15
5 % PS*****	3,4	31	3,6	29	2,0	10	21

*XAF – X-ray amorphous phase, **SA – succinic acid, ***AA – acrylic acid,

****PVA – polyvinyl alcohol, *****PS – polystyrene

Conclusions

Thus, the results of the carried out investigations showed that using carbon containing compounds as modifiers and modifying the surface of quartz particles by carbon in the course of MCT one can control the combustion process in the following SH-synthesis. The efficiency of using quartz modified in the presence of carbon containing additives is seen in the change of thermokinetic characteristics of the combustion process of the system ($\text{SiO}_2+37.5\%\text{Al}$) that results in a more complete reduction of Si and formation of highly disperse particles of silicon carbide. The phase

composition and structure provide high strength of the synthesized composite.

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