Self-Propagating High Temperature Synthesis of Composition Materials using Mineral Raw Materials

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Abstract

The possibility of obtaining multicomponent refractory composition materials on the basis of quarts containing raw material by SHS method was studied. The use of a modifying carbon additive in the form of graphite power, carbonized rice husk, apricot stones and shungit was considered. It is shown that a complex use of preliminary mechanochemical activation (MA) and modification of the charge mixture with carbon containing additives contributes to formation of carbide and nitride phases in synthesis products.

Introduction

Carbon containing refractory materials are widely used in different fields of engineering and industry due to the combination of their unigue properties, such as resistance to attack by corrosion media and abrasion, high hardness and heat conduction and others. Production of refractories by conventional technology is known to be a power consuming long process due to the use of roasting furnaces. At present, SH-synthesis allows obtaining a wide range of such materials [1-3].

One of the problems in production of carbon containing composition systems is the use of different carbon additives which are able to substitute expensive carbon. So, when producing materials by SHS technology, soot of different types, graphite powder are often used as a carbon component [2-3]. Rice husk a new and prospective source of raw materials for production of silicon carbide as it contains, apart from organic part, up to 30% of silica-silicon dioxide in its composition [4]. The most important thing is, first of all, purity and dispersity of the material being obtained from rice husk. Heating of rice husk under definite conditions in the atmosphere of nitrogen, argon or helium results in formation of silicon nitride and carbide [4, 5, 6].

Formation of carbide and nitride fibers from rice husk proceeds comparatively readily due to a number of facts: the amorphous form of silica of rice husk has a great specific surface contributing to the procedure of reactions and the admixture of iron which is always present in it server as a catalyst [6].

The search for new promising substitutes of carbon for production of carbide containing composition materials remains to be actual. The use of a cheap available raw material in production is of great interest. So, at present, utilization of rice husk, apricot stones is an actual problem which is most widely solved by thermal treatment (carbonization) [6, 7].

When obtaining materials under the conditions of SHS, an important role is played by mechanochemical activation (MA) which allows to achieve a high degree of particles dispersity, change the structure, power capacity and, consequently, provide high reactivity of the material [8-11]. Mechanical activation may effect both the rate and conditions of combustion front propagation (a macro kinetic effect) and the form and sizes of crystallites and porosity of the structure (a structural effect) [8].

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Mechanical dispersion of silicon dioxide resulting in formation of non-equilibrium fresh surface with a high concentration of broken bonds is one of the bright examples of mechanical activation [12]. Also it is known that mechano-chemical activation (MCA) of green combustible mixtures leads to formation of nano-particles (up to 100 nm in size) with high specific surface are, which enhance system's reactivity [8, 9].

Having taken quartz containing systems as an example, this work shows the perspectivity of a complex use of preliminary mechanochemical activation and modification with carbon containing additives for solution of the task on creation of new carbon containing composition SHS materials.

Experimental

Quartz of «Aktas» deposit was used as an oxide component of a charge mixture, aluminum powder of the brand PA-4 was used as a reducer in SHS processes. In the course of mechanochemical activation of quartz, carbon containing modifying additives: carbonized rice husk (CRH), carbonized apricot stones, shungite, graphite (scraps of graphite electrodes) were used.

MA of SiO_2 powders or its MCA with additives were carried out in a planetary centrifugal high power mill. Atomization in the mill occurs under the action of two centrifugal fields created by a rotating platform (up to 700 rpm) and rotating milling vessels (about 1200 rpm), which allowed to attain the centrifugal acceleration value up to 20 g.

Thermal carbonization (TC) of preliminary mechanochemically treated (MCT) SiO_2 powders was carried out at temperatures 850–860°C in a rotating quartz flow reactor with flow rate of propane-butane mixture in the range 20–50 $cm^3 min^{-1}$ with process duration of 1 h. The TC was followed by powders calcinations at $T > 900°C$ for 0.5 h.

The process of carbonization of rice husk and apricot stones was carried out under isothermal conditions in a rotating reactor in an inert medium at 300-900°C, the rate of argon supply 50 cm^3/min, the time of contact 30-60 minutes. SH-synthesis of samples was carried out in a muffle furnace at the temperature of 800-900°C. Carbon content in the mixture was determined by absorption-weighing method [7].

SHS in mixture of thus activated (carbonized) SiO_2 with Al powder was carried out in a laboratory-scale electric furnace SNOL using the pellets of different size ignited in the furnace. The furnace temperature could be varied between 700 and 1000°C. The pellets with diameter d = 15, 20, 50 mm and height h = 15, 25, 50 mm were compacted using a laboratory-scale Carver press at a compacting force of 5 t.

The combustion temperature T_c was measured with an Ircon Ultrimax Plus UX10P pyrometer (600–3000°C). The accuracy of temperature measurements was better than 1% in the range 1500–2000°C and 2% above 2000°C. In order to display the obtained results in the real-time scale on a computer screen, the device was equipped with a COM port, so that the temperature could be monitored using the standard RS-232C protocol. The time resolution of the device was 0.5 s. Besides, the ignition temperature of samples could be determined with a chromel-aluminum thermocouple linked to an HO-71.5 loop oscilloscope. As a result, we could measure the temperature, heating-up time, and reaction time and use these data to calculate the reaction rate. The degree of reaction completeness was inferred from the phase composition of products.

XRD analysis was carried out using a DRON-4M diffract meter (Co-K_α radiation) in the range of $2\theta = 10–70°$. Electron-microscopic analysis was carried out with a JEM-100CX transmission microscope (U = 100 kV).

Micrographs of the sample surface after SHS were taken with an INCA ENERGY energy-dispersive spectrometer installed on Superprobe 733 electron-probe microanalyses (accelerating voltage 25 kV, probing current 25 nA).

Results and discussion

When producing materials under SHS conditions, an important role is played by preliminary mechanochemical activation (MA) which allows to achieve a high degree of particle dimensions, to change the structure, power consumption and, hence, to provide high reactivity of the material. Mechanical dispersion of quartz which results in formation of a non-equilibrium fresh surface with a high concentration of broken bonds is one of the striking examples of mechanical activation [8-12].

An active form of a carbon additive and its uniform distribution in the volume of SHS mixture were obtained due to preliminary thermal carbonization of quartz particles composing the charge mixture of the components. Thermal carbonization gives the possibility of creating nanosized fibrous forms of carbon on the surface of mechanically activated quartz, thus contributing to the improvement of physico-mechanical indexes in the course of SH-synthesis of carbon containing refractories [9, 10]. The structure of the thermally carbonized silica powder (after preliminary MCT) is characterized (Fig. 1) by the presence of tubular carbon (of different size and configuration) on the surface of SiO_2 particles. A distinctive feature of the carbonization of silica after MCT is the formation of stitch-fiber structures with numerous inclusions (Figs. 2a-c). The preliminary mechanoactivated mixture is carbonized to a marked extent that may be associated with either the defectiveness of SiO_2 structure or the presence of iron inclusions coming from the walls of a steel vessel and milling balls during mechanical treatment [6-8]. There are a lot of metal-containing particles encapsulated into the carbon shell.

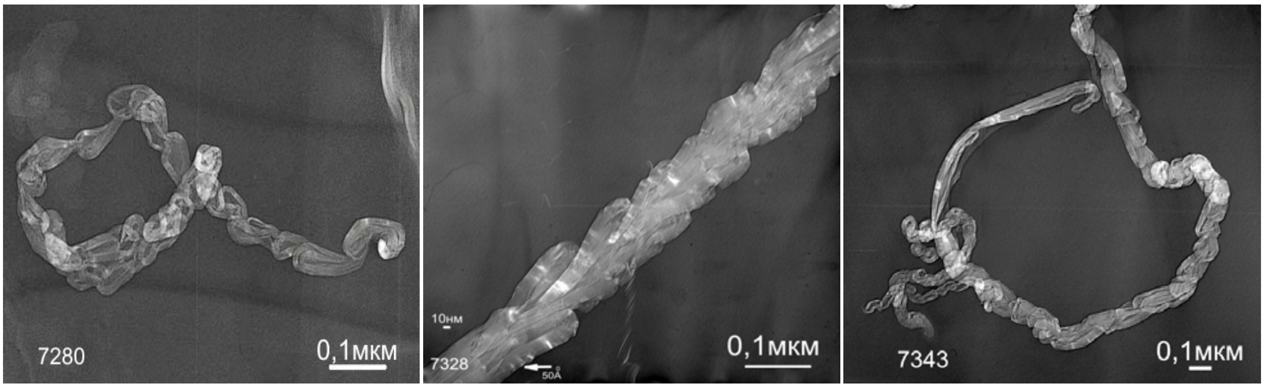

Fig. 1. EM pictures of carbon nanoparticles formed during MCT

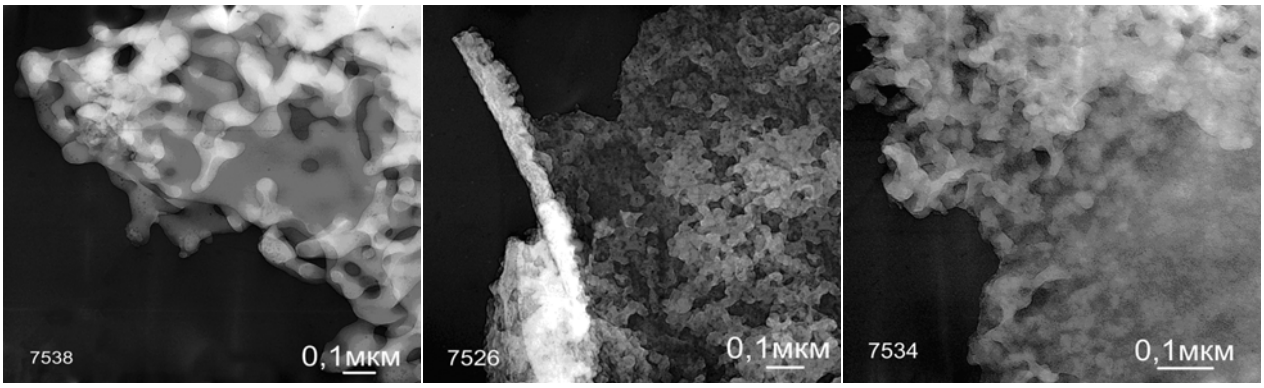

Fig. 2. Electron-microscopic pictures of the KRH sample obtained at 800°C [7]

The rigid framework (skeleton) of carbon structures renders a positive influence on the properties of SHS materials synthesized from modified batch mixtures. The structure of silica particles subjected to MCT and carbonization facilitates the reaction of SiO_2 particles with Al during subsequent SHS process.

Mobilying carbon additives in SiO_2 system were studied which provide the purposeful creation of structural and phase components of the composite, determining the necessary level of its properties. Available carbon containing additives: carbonized rice husk (CRH) shungite, graphite were used as substitutes of carbon. Thus, utilization of rice husk today is an actual the most common way to solve it being thermal processing. The choice of rice husk as a modifying additive was conditioned by the fact that it contains both carbon and silicon. The carbon content in the original sample of rice husk after drying was 35.4% wt. It is stated that the maximum carbon content for the samples of carbonized is observed at 800°C and reaches the value of 51.1% wt. Electron microscopic study (Fig. 2) has shown that the increase in the temperature of carbonization results in gradual structurization of the surface of rice husk and the emergence of nanoscale morphological formations of different types [7, 13].

Shungite carbon is highly active in redox reactions [14]. Due to extremely intensive contact between the active carbon and silicates, when heating shungite ore, there actively proceed the reduction reactions of silica to silicon and silicon carbide. As carbon modifiers in the present study we investigated shungite of "Bolshevik" deposit in East Kazakhstan region, which contains up to 66.7% carbon and 70.5% silicon dioxide, and waste of graphite electrodes.

Cylindric samples were molded from the mixture of powders of activated and non-activated silicon dioxide and carbonized rice husk with aluminum in a stoichiometric ratio of the components (62,5% SiO_2 + 37,5% Al) and 2-20 wt.% of carbon-containing additive and SH-synthesis was carried out in a muffle furnace at 900°C. SH-synthesis of the samples in all cases proceeded with evolution of gas due to burnout of carbon. Figure 3 shows the temperature profiles for a system based on quartz with 10mass.% of carbonized rice husk. Figure 3 shows that pre-MA of the charge before SHS reduces the induction period and increases the combustion rate that can be accounted for the increase of activation energy of the subsequent chemical transformation.

Besides, preliminary mechanochemical activation and modification with carbon increases the maximum combustion temperature. Similar results were obtained in the studies where graphite and schungite were used as modifying additive [10]. It is supposed that MA results in formation of a fresh surface, creation of new reaction centers and accumulation of various defects both on the surface and the bulk that activates the solid-state reactions and also creates the conditions for gas-phase and heterophase reactions. The final result of SHS of mechanically activated and modifying systems due to the peculiarities of the synthesis is a different phase composition of combustion products (Table 1).

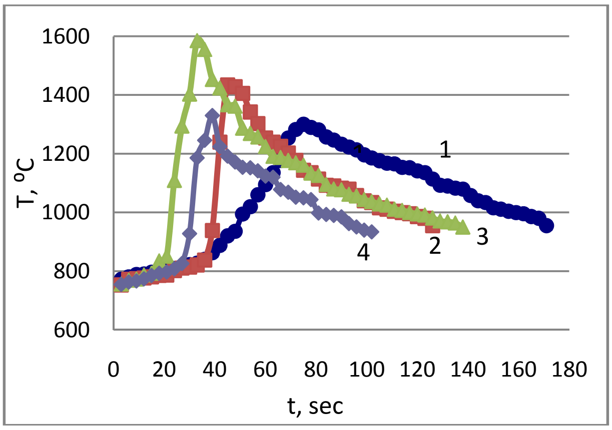

Fig. 3. The thermogram of the system SiO_2-Al-10% C (CRH) 1 – Without MCA, 2 – 5 min MA, 3 – 10 min MA, 4 – 15min MA

Table 1

Results of X-ray phase analysis of SHS products of systems SiO_2 - Al-C

samples		Content, %										
	τ, act, min	Al_2O_3	Si	cristo-balite	Al	SiO_2	AlN	SiC	$Al_6Si_2O_{13}$	$FeSi_2$	mullite	Si_3N_4
SiO_2 -Al	-	47,3	15,0	16,8	11,4	8,0	1,4	-	-	-		
SiO_2-Al-10% KRH	-	45,1	10,8	17,8	9,8	9,2	0,5	3,7	-	-		
SiO_2-Al- 10 % KRH	5	56,8	12,6	3,9	2,0	1,7	2,0	8,7	9,9	2,4		
SiO_2-Al- 10 % KRH	10	57,8	12,2	3,3	3,2	0,8	1,7	11,9	5,7	3,4		
SiO_2-Al- 10 % KRH	15	49,0	8,0	3,2	5,2	4,6	1,9	15,8	10,2	2,1		
SiO_2- Al- 10 % graphite	-	49,6	12	7,3	5,5	1,1	1,4	17,7	4,3	1,1		
SiO_2- Al- 10 % graphite	15	40,8	10,4	3,8	8,0	9,0	11,3	9,1	5,6	-		
SiO_2+Al+10масс. % shungite	-	47,4	13,7	13,4	7,9	13.4	4,4	-	-	-		
SiO_2+10масс.% shungite	10	43,9	10,5	3,9	7,0	10,2	11,3	6,3	5,6	1,3		
SiO_2-Al- 10 % CAS	10	64,3	12,9	3,4	-	5,7	-	6,4	-	-	7,3	
SiO_2-Al- 10 % CAS	20	64,9	4,6	0,6	1,2			24				4,7

As can be seen from Table 1, in SHS products one can observe, formation of aluminum nitride, silicon carbide, mullite, and their content of their increases when using pre-MA of the mixture obviously due to the completeness of reactions in the course SHS. The formation of aluminum nitride, to a greater extent after MA, is possibly related to the fact that ultrafine aluminum powder may react with atmospheric nitrogen in combustion. Iron silicide is present in the products in small quantities, of, which can be explained by "rubbing" of iron from the surface of steel vessels and balls of the planetary centrifugal mill being used [9, 13].

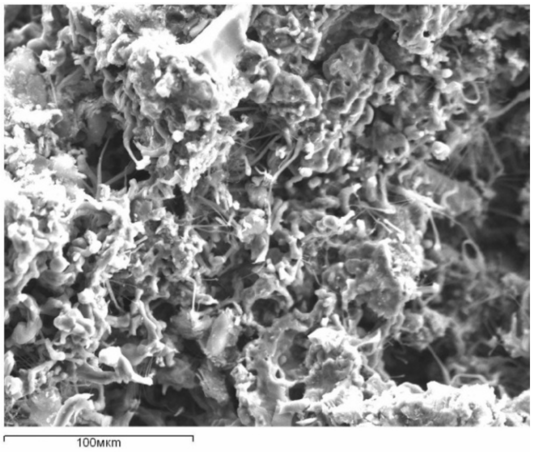

Fig. 4. EM picture of product synthesized at 900°C.

It should be noted that the use of MA and modification with carbon-containing additives in the system SiO_2 - Al enhances the strength of the synthesized material to 35-50 MPa and refractory to 1800-2000°C.

Conclusion

Thus, the main results of the studies showed that:

– SHS-composite materials based on mechanochemical silicon dioxide modified with available carbon containing additives were obtained;

– For production of SHS-carbon composite materials it is possible to use cheap raw material: carbonized rice husk, apricot stones, of shungite and wastes graphite electrodes;

– The regularities of the influence of preliminary mechanochemical activation and modification with carbon-containing additives on the development of SHS-process and final products of synthesis are stated.

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