# 2U3UUSUUF 2UUFUՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱՉԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ

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# NOVEL NANOCARBON MATERIALS FOR DIFFERENT APPLICATIONS

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This paper reviews recent results in the field of novel nanocarbon materials research obtained in the Combustion Problem Institute and their practical applications. They are:

- sorption of gold and ion of heavy metals by carbonized apricot stones;
- mechanochemical encapsulation of quartz particles in metal carbon films;
- novel carbon materials for battery application;
- multifunctional catalysts of oil hydrofining;
- carbon containing refractories;
- fullerens and nanotubes formation during hydrocarbons combustion

# Introduction

Carbon formation and growth during pyrolysis of organic substances on the surface of metal oxides and salts have been attracting the attention of specialistists dealing with the study of carbon materials for many years. It is found that the most effective catalyst of carbon formation is Fe, Ni, Co and alloys of these metal particles [1]. As a result of catalytic reaction there are formed carbon sediments on disperse metal particles. These sediments have specific forms and properties which allow considering them as perspective ultradisperse systems. The part of carbon, which forms coke, has extended in fibers tubular morphology during cracking of carbon on metal catalysts and catalyst particle proportional to fiber diameter is discovered in the head of tube.

There are conducted works on obtaining carbonized materials based on local clays and wastes of metal mining industry: chromite and bauxite sludges, agricultural wastes (rice husk, grape and apricot stones) and using them in different applications. Obtained absorption-catalytic systems are applied for purifying metals and radioactive elements, cleaning water from ions of heavy metals and radioactive elements and obtaining improved types of refractory materials, as carriers of catalysts of conversion reactions of hydrocarbons [2-4].

During production of composition systems the special attention is paid to carbon and silica. In this respect mechanochemical treatment is one of the effective methods of creating material of new quality as a result of profound structural changes including the changes of nanoscale level. Production of powder materials with nanocomposition structure of particles, especially quartz particles, capsulated as a result of mechanochemical treatment into the shell of carbon containing compounds with purposeful structural organization of surface and formation of certain complex of physico-chemical and functional properties of material being synthesized is connected with necessity to determine mechanism of mechanochemical synthesis of surface structures of nanosized scale [5, 6].

# Novel carbon materials for lithium batteries.

Electrode materials are of great interest both from viewpoint of progress in the field of lithiumion accumulators and in connection with developing technological use of carbon nanotubes [7, 8]. From the presented on the market products, lithium-ion batteries are the most perspective. Lithiated carbon (LiC<sub>6</sub>) developed by the Japanese investigators is used as an anode material in these devices [9]. Although many types of carbon were studied as materials of anodes for lithium batteries, in practice, natural or synthetical graphite is used, as this material has sufficient capacity of 372 m.A.h/g, good recharging ability and flat profiles of charge. Electrolytes based on propylene carbonate (PC), are attractive because of fine ionic conductivity at the environmental temperature. However, graphite has bad compatibility with electrolytes, based on (PC) due to interlayer incorporation of solvent leading to destroying electrode structure. Search of novel materials with improved characteristics of recycling and good compatibility with solvents of electrolytes is the most perspective. Below there are given experimental data on preparation and characteristics, obtained during electrochemical testing of carbon from apricot stone as an anode for ion batteries.

Anode material was obtained using carbonization of the shell of apricot stones. Samples obtained at 1023 K were used for creating anode after washing them with isopropane and drying at 383 K during 12 hours in vacuum cabinet. Tests of electrochemical half-elements were carried out with using different electrolytes at room temperature.

Figure 1 shows characteristics of recycling for half-elements at various numbers of cycles and with different electrolytes. One can see that carbonized apricot stone has fine stability as an anode in used electrolytes with different salts and solvents at high values of recycling.

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# Figure 1 - Cycling performances of cell Li/1 mol LiClO<sub>4</sub> in EC:DEC=1:1/CAS, 1C (a) and of cell Li/1M LiClO<sub>4</sub> in PC/CAS at 1C rate (b)

During the initial cycle, it shows higher initial irreversibility which is related to protective filmformation on the electrode surface. However, the system shows high reversibility closer to 100% cycling efficiency during the subsequent cycles which extended up to 200 cycles. In order to investigate the CAS electrode compatibility with the PC electrolyte, the system was tested using 1M solution of LiClO<sub>4</sub> in PC as electrolyte.

Electrochemical tests of the material obtained from carbonized apricot stones as an anode were carried out in cells CR2032 of coin type using method of galvanostatic recycling. It was shown that carbonized apricot stone has fine stability as an anode in used electrolytes with different salts and solvents at high values of recycling.

# Multifunctional catalysts of oil hydrofining.

Multifunctional catalysts of hydrofining were developed using modification of aluminiumcobalt-molybdenym catalyst by decationated zeolites [4]. Catalysts were prepared using traditional method of soaking. After formation catalysts were dried at 393-420 K (4 h) and pierced at 823 K for 5 hours. Prepared in this way catalysts were subjected to the process of carbonization in order to obtain active forms of carbon as a carrier. Activation of catalysts was carried out under conditions of reaction using sulphurization of free sulfur, at first at 393-423 K, at hydrogen pressure of 0.7-1.0 MPa for 3 hours, and then sulphurization was carried on at 473 K, at hydrogen pressure of 2.5 MPa for 2.5-3 hours.

Activity of catalysts was tested in laboratory flowing installation in the process of hydrofining of gasoline and diesel fractions of oil at pressure of 2.0 - 4.5 MPa, at temperature of 593 - 673 K and at volume rate of raw materials supply of 1-4 hour <sup>-1</sup>. To compare catalytical activity characteristics of  $\Gamma O - 70$  industrial catalyst were determined under similar conditions. Also the degree of hydrodesulphurization was studied on modelcompounds. Butyl –mercaptan and thiophen diluted in n-decane were used as a model compound. Isomerized activity was tested in cracking reactions of hexane and decane. Developed catalysts showed higher indexes than  $\Gamma O$ -70 industrial catalyst. Degree of hydrodesulphurozation increases from 75.3 to 98.2 %, degree of isomerization increases from 18.3 to 41.7 % with increase in temperature from 593 to 673 K. According to the data of detailed hydrocarbon analysis calculated octane number increased from 70 to 83.5 (table 1).

	Octane number	Boiling temperature	Concentration (mass %)					
			Paraffins	Naphthenes	Sulphur- containing compounds			
Initial straight- run gasoline (SRG)	70.8	88.1	21.4	12.9	0.12			
SRG after tests on CC	83.5	36.06	12.5	16.0	0.001			

Table 1 - Activity of carbonized industrial  $C_oM_o$  – catalyst (CC) on characteristics of straight-run gasoline, carbon concentration -10~%

Investigation of surface and porosity of catalysts according to the BET method has showed increase in specific surface of catalyst from 80 to 240  $m^2/g$ . Catalysts mainly have pores with sizes of less than 50 nm. Electron-microscopic investigation has showed that carbon used catalysts are highly dispersed. Size of the metal particles ranges within 20-40 nm.

#### Carbonization of vegetable raw materials.

Raw materials based on reprocessing of agricultural products refer to rapidly renewable sources and they are cleaner in ecological respect [10]. During carbonization (pyrolysis in inert medium) of the samples of apricot stones (AS), grape stones (GS) and rice husk main lost of mass occurs in the temperature range of 473-773 K. Nearly 50 % of mass is lost at 773 K for an hour.

Specific surface which reaches to 830  $m^2/g$  has been determined using method of thermal desorption of argon. Change of morphology and structure of carbon-containing sorbents depending on temperature, carbonisation time was showed by electron-microscopic method. There is a presence of complex morphological formations (figure 2), having nanoscale structure, and defining, as consequence, a high specific surface of the material.

Distinctive feature of the carbon material obtained by the carbonization of the wheat bran is formation of poorly discernible pounded particles at 723 K on the surface where unique nanotubes with a "bulb" are formed at the basis at 923 K and 1023 K. The processes, occurring in the sample lead to growth inhibition of the "bulbous" nanotubes, and their formation is not observed at the carbonization temperatures 1073 K and above, at all.

Influence of various factors (process temperature, sorption time, nature of activating agent, and pH point) on sorption properties of the synthesized nanocarbon materials for the caesium-137 (<sup>137</sup>Cs), strontium-90 (<sup>90</sup>Sr), lead-210 (<sup>210</sup>Pb) and ions of toxic metals (Sn, Ni, Cd, Cr, Zn, Au) was investigated.



Figure 2 - The electron microscopy images of WB, carbonized at: a) 723 K (nucleuses position); b) 650°C (the beginning of the "bulbous" nanotubes growth on a sample); c) 1023 K (mature nanotubes on the edge of WB sample)

It was noted, that all investigated elements are quantitatively sorbed by activated sorbent for the first 5 minutes and sorption degree doesn't depende on the carbonization temperature under the present experimental conditions.

Table 2 shows dependence of the sorption degree on the pH of solution at the various carbonization temperatures for sorbent, activated by water stream, but, displaying, nevertheless, the general character of dependences for the sorbents, activated by the hydrogen peroxide  $(H_2O_2)$  and ammonia  $(NH_3)$ .

	РН										Carboni-
Ele-	1.5	3	4	6	7	8	9	10	11	11.5	zation
ment	Sorption degree, %									tempera- ture, K	
Sr	37.0	40.1	48.0	56.7	55.2	66.7	69.7	69.4	70.2	70.5	
Cd	18.8	81.1	83.2	92.6	92.6	98.7	99.5	100.0	99.3	100.0	272
Cs	16.1	73.9	73.6	73.6	74.2	74.0	74.2	74.0	74.1	74.0	115
Pb	12.8	81.0	93.4	99.3	99.2	100.0	100.0	100.0	100.0	100.0	
Sr	35.8	48.0	51.6	57.5	60.4	59.7	64.9	65.0	65.7	-	
Cs	17.0	76.5	76.4	75.9	74.8	76.4	76.2	76.5	76.8	-	873
Pb	13.1	84.4	90.9	97.7	99.2	100.0	100.0	100.0	100.0	-	
Sr	37.5	44.6	49.0	63.4	61.9	63.4	75.3	76.3	76.6	74.1	
Cs	19.8	79.0	78.8	79.1	78.4	78.8	79.0	78.5	78.3	78.8	973
Pb	22.8	92.0	93.2	98.6	99.0	100.0	100.0	100.0	100.0	100.0	
Sr	36.7	43.0	50.5	64.7	66.4	69.2	72.0	72.0	-	-	
Cs	15.0	75.4	78.3	79.4	79.3	80.8	80.0	80.0	-	-	1073
Pb	12.0	83.0	95.1	98.8	100.0	100.0	100.0	100.0	-	-	

Table 2 - Dependence of the sorption degree of radioactive isotopes on the pH and arbonization temperature of WB, activated by water. Sorption time - 30 min

Mechanism of sorption of ions of heavy metals by carbonized sorbents was found by physicochemical methods of analysis. Carbonized sorbents were found to be effective during absorption of ions of heavy metals and radioactive elements and also gold separation from alkaline solutions.

# Fusicoccine extraction on novel carbon-mineral sorbent.

In nanocarbon materials laboratory of Combustion Problem Institute carbon-mineral sorbent (sorbent carbonized from vegetable raw materials –2) based on carbonised raw materials, which contain carbon and silicon oxide and also has nanosized morphology, has been synthesized [11]. This material has specific and unusual properties due to presence of these components. If carbon is hydrophobic material and silicon oxide is hydrophilic one absolutely new combination of hydrophobic-hydrophilic properties emerges. These unusual properties allow offering the given material as a unique nanostructurized sorbent for separating bioorganic compounds.

Sorbent carbonized from vegetable raw materials -2 was synthesized by carbonisation of vegetable raw materials in rotating steel reactor in the temperature range of 573-1073 K for 5-60 min in inert medium. It was found that specific surface of samples increases with increase in temperature reaching maximum at 923 K (920 m<sup>2</sup>/g) and then decreases.

To separate fusicoccine the technique developed in M.A. Aitkhozhin Institute of Molecular Biology and Biochemistry was used [12]. Taking into account tough climatic conditions of Kazakhstan it was very interesting to study action of biostimulator on stress resistance of the most important grain crops of Kazakhstan. So we studied action of purified fusicoccine on germinating capacity of seeds of wheat of *Nadezhda sort* by adding 2 % of NaCl, that creates condition of strong chloride salinization. Experimental results are presented in table 3. As follows from the table 3, fusicoccine increases germinating capacity of seeds under by 19 % conditions of salinization. Also fusicoccine increases root system of a plant.

Variants	% of germination				
2.2% NaCl	67				
2. 2% NaCl+MЦ	86				

Table 3 - Action of fusicoccine on of the seeds of Nadezhda sort wheat

The experiment carried out in the Scientific-industrial center of agriculture and plant growing of the Republic of Kazakhstan in 2004-2005 has showed that application of biostimulator for increasing winter resistance of winter wheat is very promising.

The carried out experiments have showed that application of biostimulator increases mass of 1000 grains by 15 % and productivity by 10%. In the course of further test there were carried out field trials of fusicoccine. The wheat treated by biostimulator was noted to ripen 15 days earlier than the wheat without treating with biostimulator (green sprouts).

One can say with great confidence that application of preparation will allow:

- 1. accelerating the ripening of wheat, i.e. to start harvesting two weeks earlier;
- 2. increasing yield in average by 15 %.

#### Sorption of gold by carbonized apricot stones (CAS) and rice husk (RH).

Carbonization of apricot stones (CAS) and rice husk (RH) was carried out by method [3]. Synthesis of sorbents by carbonization of this agricultural raw materials in the temperature range of 673 – 1073 K in a nitrogen atmosphere for 30 min was investigated. Carbonized sorbents based on apricot stones have a code: CAS-1; CAS-2; CAS-3 and carbonized sorbents based on rice husk have a code: RH-1, RH-2, RH-3. Sorption of gold (III) was studied by electrochemical method on potentiostate P-5848 by the means of recording J-t-curves at constant potential corresponding to extreme current of gold electroreduction (III).

Carbonized sorbents based on vegetative raw material concurrently possess ion-exchanging and reducing properties. Stationary potentials of CAS were measured to reveal their reducing properties. The sorbents of CAS series have relatively low oxidative-reducing potential that in dependence on CAS mark change in range from 0.20 V to 0.25 V.

Measured stationary (real) potential [A $\mu$ CLI] muriatic medium is 0.76 V. Difference of potentials between gold-oxidant and sorbent-reducing agent is 0.51-0.56 V. Difference of potentials of 0.24 V is required for practically complete passing of any oxidative - reducing reaction. As follows from these data there is a real opportunity for reducing of gold (III) to metallic state. This opportunity is proved by magnitudes of CAS sorbent potentials after sorption of gold (III) on it.

The results on sorption of gold (III) with RH sorbents in 0.25 N HCl solution using a common method [13]. As it is seen (figure3), RH-1 exhibits the best 100 % sorption capacity with respect to gold (III).



Figure 3 - Kinetic curves of sorption of gold (III) on different sorbents in 0.25 N HCl solution. Mass of the sorbent is 0.2 g, the amount of gold (III) is 0.6 mg, the volume of the solution is 25 ml. Sorbent: 1 – RH-1; 2 – RH-2; 3 – RH-3

The sorbent RH-2 absorbs about 60 % of gold (III) during 1 hour, and the sorbent RH-3 only absorbs 20 % of gold (III) during the same period of time. In the case of sorbent RH-1, a complete,

practically 100 % sorption is observed within 4 minutes. The shape of the kinetic curves also shows the decrease in the rate of gold (III) sorption as follows: RH-1> RH-2 > RH-3.

During sorption of gold (III) the grains of RH-1 sorbent are covered by a film of yellow color which is a metallic gold according to electron-microscopic pictures (figure 4, 5).



Figure 4 - Microphoto of sorbent RH-1+Au (III)

Figure 5 - Microphoto of sorbent CAS-3+Au (III)

The reducing ability of RH sorbents was verified by the measurements of the values of stationary potentials of these materials, which were carried out with the help of electrode of special construction. This electrode is a fluoroplastic casing with the diameter of 20 mm with a thread at the end face, where platinum electrode with the diameter of 19 mm is fixed. A platinum current collector is brought out from the platinum electrode through the center of the casing. The platinum disk is compressed by a fluoroplastic clutch with a perforated face. When measuring the potential, an ash-free filter is placed on the perforated face, the sorbent that being studied is poured onto the filter. Then the clutch with the sorbent is applied by winding on the fluoroplastic casing, thereby providing an intimate contact of the substance being studied with the platinum electrode. The results of the measurements showed that the sorbents of RH series have a quite low redox potential. The sorbents RH have reducing properties, which are likely to be conditioned by the presence of the carbonized sorbents of reducing carbon groups: aldehyde, ketone, alcohol groups on the surface. Besides, carbon itself may possess reducing properties, the more so, as it is in the form of nanocarbon tubes [13, 14].

The best sorbent is RH-1. The complete (99-100 %) extraction of gold (III) on this sorbent takes place during 3.5–4 min regardless of the initial content of gold (III) in solution. The sorption time of the half of the initial content of gold (III) -  $\tau_{1,2}$  is 1.1 min irrespective of its initial concentration, the sorption rate obeys the first order kinetics law (table 4). This order of the reaction is characteristic for the electrochemical process limited by the substance to the surface of the electron donor.

N⁰	Concentration of Au (III), mg/l	W, mg/c·g (of the sorbent)	$\tau_{1/2},$ min	$K_{s}, s^{-1}g^{-1}$
1	5.97	$0.54 \cdot 10^{-2}$	1.18	$7.35 \cdot 10^{-2}$
2	11.95	$1.08 \cdot 10^{-2}$	1.10	$7.15 \cdot 10^{-2}$
3	23.90	$2.26 \cdot 10^{-2}$	1.12	$7.45 \cdot 10^{-2}$

Table 4 - Kinetics of gold (III) sorption on RH-1 sorbent in 0.25 N HCl solution

The dynamic sorption capacity of RH-1 sorbent was determined, i.e. the capacity before passing of gold (III) ions through the adsorption column. The passage rate of gold (III) solution with the concentration of 23.9 mg/l was 2.5 ml/min, the amount of the sorbent taken was 0.5 g. The experiments showed that passing of gold (III) ions took place after passing of 220 ml of gold (III) solution that corresponds to the sorption capacity of this sorbent – 10.5 mg of gold / 1 g of sorbent. In the case of sorbents RH-2 and RH-3, when passing the first portion of gold (III) solution of 25 ml, the passing of 60-70% of the initial amount of gold (III) is observed. The sorption capacity of these sorbents is lower by two orders of magnitude than that of the sorbent RH-1 [15-17].

The dynamic sorption capacity of sorbent RH-1 with respect to gold (III) is 10.5 mg/g of the sorbent. The capacity of sorbents RH-2 and RH-3 is by two orders of magnitude lower. The presence of excessive amounts of Ni (II), Co (II), Cd (II), Zn (II), Cu (II), Fe (III), Pt (IV), Hg (II), As (V) does not interfere with the sorption of gold (III). Extraction of metallic gold occurs non-uniformly on a whole surface of CAS particles, and in separate areas where the growth of gold crystals occurs. Hence, the process of metallic gold extraction and sorbent reducing groups oxidation is electrochemical, i.e. there are cathode and anodic areas. Cathode areas are formed in initial moment of sorption where further the reducing of gold (III) occurs.

The increase of gold (III) sorption velocity occurs in presence of copper salt (II) and iron (III) that is connected to catalytic effect of gold (III) reducing. Complete sorption of gold (III) occurs for 5 minutes in the case of presence of copper (II) ions, and in the case of iron (III) - for 1.5 minutes, when in absence of these admixture - for 8 minutes. The dynamic sorption capacity of sorbent RH-1 with respect to gold (III) is 10.5 mg/g of the sorbent. The capacity of sorbents RH-2 and RH-3 is by two orders of magnitude lower.

# Mechanochemical encapsulation of quartz particles in metal carbon films.

Mechanochemical synthesis has great advantages compared to other methods in the production of highly disperse nanostructural materials based on silicon containing materials. As it was shown [5, 6], by mechanochemical synthesis it is possible to obtain quartz-based highly disperse materials which exhibit simultaneously magnetic, dielectric and electric properties depending on the regimes of treatment and the conditions of subsequent application.

It is found that there is a certain regularity in the structural transformations taking place on the surface of a quartz particle with the carbon of organic additives during the treatment of the material in a mechanical reactor: from thin dense films with the introduced ultradisperse particles of iron to

porous multiplayer structures with the formations of different configurations grafted to the surface of particles.

Complex investigations of changing structure, state and properties of quartz depending on regimes of mechanochemical treatment without participation and in presence of modifiers have showed that change of the structure of quartz particles in the process of dispersion is of periodical character [5-7] that reflects in the change of their characteristics both macro-, micro- and nanolevels including change of defective structure of their surface layers and size of crystallites (blocks of coherent scattering). It is found that time of the most considerable structural changes is 20 and 45 min under the conditions of the experiments being carried out simultaneously at all considered levels. Result of structural changes during mechanochemical treatment is the change of energy substance state.

It is found that during mechanochemical treatment use of organic additives intensifies effect of modification of quartz particles. It is shown in increasing specific surface, specific volume of pores and decreasing density of powder material, i.e. in significant structural changes of surface layers of quartz particles being dispersed (table 5). Calculation of modification degree of quartz powder has showed that butanol, acrylic acid and polystyrene are effective modifiers providing change of structure of from 30 to 70 % and more of volume. Novel morphological structures are synthesized on the surface of quartz particles, which plays the role of matrix for creating composition powder systems.

Marcal	<b>G</b> 2/	<b>N</b> 3/.	ρ, g/	ζ,				
Material	$S_{sp}$ , m /g	v <sub>sp</sub> , cm/g	$(\rho_{each})$	(ρ <sub>π</sub> )	%			
SiO <sub>2</sub>	5,20	0,11	2,55	2,65	-			
SiO <sub>2</sub> +5%C <sub>2</sub> H <sub>5</sub> OH	5,24	0,18	2,03	2,06	17,1			
SiO <sub>2</sub> +5%C <sub>4</sub> H <sub>9</sub> OH	6,50	0,32	1,67	1,69	32,4			
$SiO_2+5\%C_2H_4(OH)_2$	10,50	0,24	1,59	1,70	25,8			
SiO <sub>2</sub> +5%C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub>	15,20	0,29	1,46	1,69	18,5			
SiO <sub>2</sub> + 5%C*	77,60	0,72	0,88	0,91	72,7			
SiO <sub>2</sub> +5%AC**	56,6	0,23	0,82	0,94	74,0			
SiO <sub>2</sub> +5%PS***	41,0	0,30	0,65	0,67	72,5			
SiO <sub>2</sub> + 10%PS	46,7	0,36	0,58	0,62	73,0			
SiO <sub>2</sub> +5%PS+1%NaCl	54,3	0,47	0,73 0,77		74,0			
*C – activated coal, **AA – acrylic acid, ***PS – polystyrene								

Table 5 - Specific surface (S<sub>sp</sub>), specific volume of pores (V<sub>sp</sub>), density ( $\rho$ ) and degree of modification ( $\zeta$ ,) of quartz powder

Electron-microscopic analysis has shown that quartz particles in initial state are dense crystals with clearly shown edges (figure 6a). After mechanochemical treatment particles modified by butanol have nondense, laminated carbon saturated structure of 10-40 nm thickness where are dense ultradisperse inclusions of iron and its compounds (figure 6b). Modification of quartz particles with both polyatomic and acrylic acid in the process of mechanochemical treatment results in formation of dense sufficiently homogeneous organic film on the surface and presence of highly disperse crystallites in surface polymeric layer. Microdiffraction pattern from surface layer of particles indicates that it belongs to carbonaceous substance with three dimensionally ordered structure. During variation of modification conditions electron diffraction picture show the presence of metal-silicon-carbon compounds or weakly crystallized silicon-carbon substance.



Figure 6 - Electron-microscopic images and electron microdiffraction of quartz particles in initial state (a) and modified in the presence of butanol (b), acrylic acid (c,d) and polystyrene (e-h)

When using polystyrene as a modifier depending on amount of modifier being used (from 3 % to 10 %), time of treatment and also during variation of force conditions of action there are formed structurized or tracery films cross-linked with a particle surface or rolled up in the form of tubes of a different configuration the size of which reaches 50-70 nm (figure 6 f-g). Increase in time of treatment finally leads to coagulation of dispersed particles with modified surface layer and formation of dendrite-like formations (figure 6h). Main element involving in building nanostructurized objects during mechanochemical treatment is carbon. Distinctive feature of carbon nanostructures on quartz surface subjected to mechanochemical treatment in the presence of polystyrene is the presence of texture i.e., favourable orientation of carbonaceous particles inside film formations (figure 6 c, d). Maximal amount of fixed carbon - 2.6 % on the surface of quartz particles was discovered in the samples modified by polystyrene which showed the most diversity of structural forms.

IR-spectra showed decrease in intensity of low frequency both valence and deformation fluctuations and increase in high frequency fluctuations. Dehydration of the surface of particles and shift of all spectra to the region of high frequencies are observed. This data testifies about that during quartz grinding there are accumulation and redistribution of defects. It results in intensifying disordering of lattice, increasing quantity of groups with weak bonds.

After modifying treatment of quartz with organic additives changes of quartz matrix spectrum affects all absorption bands: polystyrene presence results in decrease of intensity and butanol on the contrary to their considerable increase. Transformation of spectrum kind affects only region of frequencies of valence fluctuations (999-1186 cm<sup>-1</sup>). There is degeneration of bands of 1162 cm<sup>-1</sup> and 1062 cm<sup>-1</sup> and shift of middle band to lower frequencies (to 1109 cm<sup>-1</sup>). Absorption bands of higher than 1400 cm<sup>-1</sup> which are caused by the presence of carbonate and carboxylic groups of different isotope composition on the surface of Si-O-Si are of special interest.

Directivity of chemical conversion of quartz particle surface during mechanochemical treatment is determined by emerging the whole complex of reaction centers with nonsaturated valency bonds. These are sililine  $\equiv$ Si<sup>°</sup>, =Si<sup>°</sup>, silanone  $\equiv$ SiO<sup>°</sup> and peroxide centers  $\equiv$ SiOO<sup>°</sup> and also silanol centers  $\equiv$ SiOH and deformed siloxane groups [ $\equiv$ Si-O-Si $\equiv$ ]<sub>def</sub>. Final products of destruction (mechanocracking) of all additives – modifiers being used in the work are radical groups H<sub>3</sub>C<sup>°</sup>, H<sub>2</sub>C<sup>°</sup>, OH and also H and C during interaction of which with active centers of quartz surface in a complex capsulation with preservation of surface defects of structure is possible.

Change of structure being grinded by quartz particle at all hierarchical levels (from particle volume to distortions within crystal lattice) is determined by the kind and degree of kinetic energy dissipation transferred to the particle at the moment of the shock with a ball and fixed in it in the form of elastic energy of deformed crystal. The structure of the quartz particle surface layer after a mechanochemical treatment may be interpreted as a nanostructural formation containing carbon, silicon, iron and having a complex structure encapsulating a particle. Finally, a composition material is formed consisting of carbon surface layer with introduced inclusions of iron, transition amorphized layer on the basis of silicon and a crystalline quartz base.

Such structural rearrangements of the surface layers of the quartz particles being dispersed result in the change of physical properties of the material. The measurements of specific resistance

of quartz powder after a mechanochemical treatment showed its decrease by more then an order of magnitude. The modified quartz powder after a mechanochemical treatment also exhibits magnetic properties (table 6).

Material		spec ρ	cific resistance, $\times 10^6$ , $\Omega \times m$	magnetic	Both		
		The ti	me of weathering,	the tim	electric		
		1	$t_{s1}$ , 24 hours	t	t <sub>sb</sub> 24 hours		
		0	30	0	30	magnetic	
Ouartz		1.1	6	2.0	2.0	characteri	
Ouartz	+	6.0	15.0	4.0	3.2	stics of	
Ouartz	+	2.5	3.5	29.0	27.0	mechanoc	

 

 Table 6 - The change of specific resistance and magnetic permeability of quartz powder depending on the time of weathering. Grinding was carried out during 5 minutes

hemically treated quartz change with time, *i.e.* the material "ages". However, if such "aged" material is placed into an electromagnetic field of definite intensity, its ferromagnetism and conducting characteristics are recovered, it being the result of interaction of a piezoelectric quartz nucleus and a carbon nanostructural film containing ultradisperse inclusions of iron.

# Carbon-containing refractory materials.

Carbon-containing refractory materials are obtained using various methods. Incorporation of chromite sludge increases density and mechanical strength in comparison with refractory material "Furnon – XII" insignificantly rising refractory property. Improvement of physico-chemical refractory materials based on clay and carbide of metals is explained by formation of fibrous carbon and carbides of metals [4]. Obtained refractory materials have high sludge resistance, that makes prediction of their use in metallurgical processes of production of precious metals possible.

Composition refractory materials obtained by selfpropagating high temperature synthesis (SHS) have a number of advantages due to their physico-chemical and operational properties as well as power consumption in comparison with conventional composition systems [18,19]. The quality of the material depends on the conditions of synthesis and possibility to control the process and, finally, on its structure and properties. One of the effective methods of influencing SH-synthesis is the use of preliminary mechanochemical activation which changes the chemical activity of reagents, thermodynamics and kinetics of subsequent thermal processes [20]. Treatment of quartz with different organic additives provided modification of the surface of particles. The difference in the morphology of the surface of modified material (quartz) depending on the modifying additives being used was found [5, 6, 21]. In case of using alcohols, in particular butanol, under the conditions of mechanochemical treatment, the surface of particles is carbonized. The degree of structural organization of carbon containing formations depend on many factors, including the time of the mechanochemical process. Nanosized formations grafted to the surface and containing carbon compounds are formed on the surface of particles (figure 6).

При использовании в качестве модификаторов других соединений, в частности азотсодержащих; ammonia(NH<sub>4</sub>OH) and acetamide (CH<sub>3</sub>CONH<sub>2</sub>) – the structure of modified particles has a number of peculiarities. There are observed filmy, platy, platy-veil and fibrous-veil structures containing nitrogen in modified quartz samples during mechanical treatment with nitrogen-containing compounds (figure 7).



Figure7 - Electron –microscopic pictures of quartz particles after mechanochemical treatment in the presence of 10% CH<sub>3</sub>CONH<sub>2</sub> (a) and NH<sub>4</sub>OH (b)

The peculiarities of the structure of modified quartz are responsible for specificity of the following processes of interaction of quartz particles with aluminium under the conditions of SH-synthesis. A definite role in these processes is played by carbon which saturates the surface layer in the process of mechanochemical modification. For quartz which was not subjected to mechanochemical treatment, the amount of carbon is 0.08 %. After treatment, the content of carbon in the sample makes up from 1.14 to 2.96 % depending on the modifying additive being introduced. Temperature of combustion of modified quartz with aluminium reaches 2473 K [22]. High combustion temperature form may be accounted for the fact that SiO<sub>2</sub> is reduced not only by aluminium, but also by H, C, CO. These reducing agents are decomposition products of compounds on the surface of quartz particles obtained when treating them with organic additives. It is known that carbide formation reactions give high temperatures in combustion processes. Besides SiC, small amounts of AIC and FeC were registered. The presence of iron compounds in the phase composition of sample being synthesized is due to the uptake of ultradisperse iron particles into the quartz powder from the walls of milling vessels and balls in the process of grinding.

Size variations of synthesized samples on the basis of the system (SiO<sub>2</sub> + 37.5% Al) with quartz modified by mechanochemical treatment in the presence of different organic compounds showed that scale factor is an effective way of influencing the course and final results of SHS-process. The diameter of samples varied from 15 to 59 mm, the volume – from 3 to 98 cm<sup>3</sup>. In SHS-systems of samples with activated quartz, the size factor exerts influence not only upon the combustion temperature, but also upon the final result of synthesis, i.e. reaction products. On samples of greater volume there takes place maximum reduction of Si and formation of sialon (it being of two types: Si<sub>2</sub>Al<sub>3</sub>O<sub>7</sub>N and Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub>) in synthesis of which nitrogen of air takes part (table 7). The content of sialon in coarse-grain samples is 18 %. This fact is of great importance, for it indicates the change in combustion kinetics, diffusion rate and the sample structure depending on the volume of the sample. Gaseous phase reactions play a significant role in the formation of phases and structure of such samples. The final results of the peculiarities of combustion of volume samples are the changes in their density and strength. The density values decrease with the time of activation, but the presence of a modified layer on the surface of quartz particles contributes to considerable increase in density (by 20 - 25 %) and strength of the synthesized material (by 50-80 %). Material containing nitrite compounds has also higher indexes of thermal-protective characteristics.

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N⁰	$\tau_{ac}m$	d/ h,	$SiO_2$	Si, %	$Al_2O_3$	$3Al_2O_3$	FeSi <sub>2</sub>	SiC	AlN	$Si_2Al_3O_7N$	XAP**
	in.	mm/mm	%		%	$2SiO_2$	%	%	%	%	%
						%					
0	0	20/20	3.5	21.0	22.0	4,0	1.0	I	1	-	48.5
Ι	10	20/20	2.2	23.8	27.5	8.6	2.4	-	I	-	35.5
Ι	20	20/20	5.0	30.0	22.0	17.0	3,5	I	1	-	22.5
Ι	10	50/50	-	24.6	18.7	10.5	1.9	-	2.1	12.0	30.2
II	10	20/20	3.4	17.6	60.5	-	6.5	-	3.0	-	9.0
Π	10	50/50	-	20.0	53.5	1.4	7.0	-	0.5	7.0	10.6
III	10	20/20	7.8	20.5	30.0	5.7	3.2	5.8	5.0	-	22.0
III	20	20/20	3.4	29.0	31.0	3.6	2.0	10	2.0	-	19.0
III	10	50/50	5.7	21.2	38.5	3.0	1.0	5.0	0.3	9.3	16.0
IV	10	20/20	1.6	20.0	50.4	4.5	7.9	6.1	5.0	-	4.5
IV	10	50/50	-	25.0	38.1	-	6.5	5.7	2.0	15.7	7.0
IV	20	50/50	-	30.0	37.0	-	3.0	5.0	-	18.0	7.0
0-	(SiO	2+37.5%	Al)	II	I - [SiO <sub>2</sub> -	+PS*]act. +3	7.5%Al				
I-	$[SiO_2]act. +37.5\%Al$ IV - $[SiO_2 + 37.5\%Al + PS^*]act.$										
II -	- [SiO <sub>2</sub> +37.5%Al]act. PS* - polystyrene										
	XAP** – X-ray amorphous phase										

Table 7 - The phase composition of synthesis products depending on the conditions of pretreatment of quartz at 1173 K

Thus, the process of mechanochemical treatment, the kind of a modifying additive and the size factor is an active instrument in creation of the material of the necessary quality. Sialon containing ceramics of the necessary composition may be obtained by SH-synthesis in the usual atmosphere of air using preliminary activated and modified quartz by varying the conditions of treatment and the sizes of the sample being synthesized as a result of active interaction of aluminium with nitrogen of air, similar to the prosses studied in [23, 24]. In using loading SHS – the mixture of quartz modified by nitrogen-containing compounds: ammonia and acetamide – amount of nitride phases in combustion products increases to 40 % and more.

#### Fullerens formation in hydrocarbon flames under electric field.

Influence of the direct electric current of different polarity on flame forms, soot yield, parameters of soot samples microcrystals ( $L_a$ ,  $L_c$  and doo2) and soot particles sizes in intensity range from 0.5 to 20 kV at electrode systems «needle-plane» at combustion of benzene-oxygen mixture at the ratio C/O=1.0 with addition of 10 % volume of argon at pressure 40 Torr was investigated [25]. It was found that at positive polarity action of electric field rises to such a degree that at U>10 kV it leads to flame extinction. It is shown that maximum decrease in soot yield is observed at negative polarity. It was found that intensity range of electric field in which soot yield was 10 % more soot yield without applying electric field. It was shown that parameters of soot micro crystals on average remain constant irrespective of intensity and polarity. Fullerenes C6o, C70 and PAHs were identified in the extracts of soot samples by the method of IR-spectroscopy.

Soot obtained under various conditions was extracted by the method of cold extraction in the medium of benzene ( $C_6H_6$ ) during 72 hours. For extraction of soot was from soot tank. The extract had sated dark red color. A solution of obtained extract was investigated by using IR-spectrometer. Figure 8 presents spectra of soot extracts that obtained at various type of electric field discharge.



Figure 8 - IR-spectra of dry extracts: 1- standard sample of fullerenes  $C_{60}$  and  $C_{70}$ ; 2 - dark discharge, U=0.5 kV, I=5×10<sup>-7</sup> A; 3 - glow discharge, U=10 kV, I=2×10<sup>-3</sup>A; 4- glow discharge applied directly on flame front, U<sub>n</sub>=7 kV, I=4×10<sup>-3</sup>A; 5- abnormal glow discharge applied directly on flame front, U<sub>n</sub>=7 kV, I=7×10<sup>-3</sup> A; 6 - without applying electric field

It is experimentally found that yield of fullerenes significantly starts to grow ( $\alpha \ge 13\%$ ) in the area of the abnormal glow discharge at values of discharge current I=7×10<sup>-3</sup> A (figure 8, curve 5), at direct applying electric field on flame front. The analysis of absorption spectrum (figure 8, curve 5) shows, that the lengths of waves corresponding to fullerenes C<sub>60</sub> ( $\lambda$ - 528, 577, 1183, 1429, sm-1) and C<sub>70</sub> ( $\lambda$  - 458, 535, 565, 578, 642, 674, 795, 1134, 1414, 1430, 1460, sm-1) are all shown, without exception, except for fullerenes in extract there was a mix of polycyclic aromatic hydrocarbons (PAH). Such connections as pyrene, fluoranthene, coronene, anthracene 1.12- bensperylene have been identified.

Identification of fullerenes  $C_{60}$  and  $C_{70}$  has been conducted by radiographic method during analysis of dry extract thin layer. For this purpose, obtained extract of fullerene containing soot from soot tank, was evaporated on a quartz support and, formed dry residue was investigated by using diffractometer. The analysis of X-patterns of soot samples of dry extracts has shown presence of peaks on reflection angle, peculiar to fullerenes  $C_{60}$  and  $C_{70}$ . Peaks, according to card file ASTM, correspond to following crystal fullerenes phases: orthorombic, cubic and hexagonal ( $C_{70}$  only hexagonal). Herein, intension ratio is not observed, that is peculiar to amorphous state of fullerene containing dry extract formed as a result of presence in the extract of polycyclic aromatic hydrocarbons.

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