# STAGE CHARACTER OF GROWTH OF CARBON NANOSTRUCTURES DURING CARBONIZATION OF SILICATE SYSTEMS

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*Carbon, quartz, nanocomposite systems*

## Introduction

At present, creation of different nanomaterials and development of new types of nanotechnologies are tasks of high-priority importance. Nanomaterials and nanostructural systems - it is a field of scientific searches and practical implementation of their results which allowed revealing another side of inexhaustible opportunities of natural phenomena and processes (Buchachenko A.L.2003, Tretyakov Yu. 2004, D., Lyakishev N.P. 2002). As a part of material sciences, chemical physics and physical chemistry are fundamental at developing methods of the synthesis of nanosystems of different structural forms and compositions which are characterized by new complex of properties and specific practical application, respectively.

Different materials and techniques are used during synthesis, however, composition systems based on carbon and silicon are preferred because both carbon and silicon are basic elements at creating different polymer systems. Their common peculiarity is a presence of strongly developed surface and consequently, presence of increased level of free energy system. Natural desire of such systems to reducing energy leads to developing naturally occurring processes providing formation of new structures both inside particle and their space interaction between each other (Gibbs D.B. 1982), that finally defines specific character of the material. Properties of surface nanostructures and specific surface are main characteristics of adsorbents and catalysts. Analysis of microstructures elucidates many peculiarities of the properties of the composite substances being obtained and also kinetic aspects of their synthesis.

One of the methods of nanomaterial creation is mechanochemical synthesis (MCS) when powders of different dispersity and structure of surface layers of particles are obtained as a result of intensive force action (Molchanov V.I. 1981). Change of environment and composition of the material being treated allows forming on the surface of the particle of different compounds of nanostructural scale and provides production of various by properties systems. Specific character of polymer structures on quartz surface is conditioned by the presence of metal atoms and by that quartz is a good piezoelectric. Electric polarization of particles during mechanical interaction promotes polarization of the surface. On the other hand, creation of closing resilient shell on the surface of the strained quartz particle allows fixing strained state, i.e. counteracts the process of relaxation and annihilation of defective structure. As a result of that obtained materials can exhibit simultaneously magnetic, dielectric or electric properties (Gibbs D.V. 1982, Gubin S.P. 1999, Saito R. 1998).

Similar by chemical composition silicon-organic composites are obtained with the method of carbonization silicon-containing systems during synthesis of sorbents of different type. Both vegetative (for example, rice shell) and mineral (clay) raw materials are used as matrix. Zeolite modified by metals of iron group are often used for obtaining sorbing substances. Elements of this group are ferromagnetics and capable to initiate formation of tubular particles with a diameter corresponding to the size of ferromagnetic particle – embryo according to magnetic mechanism (Biisenbaev 2004). Process of carbonization is associated with emerging defects – active sites in matrix and their interaction with catalytically modified carbon forming from carbon-containing atmosphere of the reactor. The result of this process is the synthesis of morphologically different carbon nanosized particles and formations.

Distinction of morphological structures of carbon particles in the materials obtained with these methods can be explained by different energy saturation of initial matrixes involving in the reaction with carbon.

The objective of the present investigations was to create composite material on the basis of combining two methods of synthesis, obtain energy saturated metal-containing matrix of silicon dioxide with mechanochemical activation, synthesize carbon particles using carbonization and investigate morphological peculiarities of formed nanoparticles.

## Experimental

Quartz ($\alpha$-$SiO_2$) with a purity of 99.8 % was taken for mechanochemcial synthesis. Quartz dispersion was carried out in the mill of centrifugal-planetary type (mechanical reactor) (Mansurov Z.A. 2006). Magnitude of acceleration during treatment in centrifugal reached 20 g. Obtained material was carbonized in revolving quartz reactor in the flow of carbon gas at the temperature of 750 $^o$ C by standard methods (Biisenbaev M.A. ). Aluminosilicate material (zeolite) was subjected to carbonization without preliminary activation.

Electron-microscopic analysis of synthesized samples was conducted on JEM-100 electron transmission microscope with a voltage of 100 kV. Samples were prepared by optimal for the given case methods of dry preparation.

## Results and their discussion

***1. Method of mechanochemcial synthesis***

In the process of dispersion of initial quartz (fig. 1a) in mill-activator particle is not saturated with defects changing energy state of a material and consequently its chemical activity regarding to reagents being introduced into the reactor. Investigations of changing structural characteristics of the material being investigated - quartz have showed that accumulation of defects inside particle leads to reducing the size of crystallites which form it and amorphization of the surface (fig. 1b). Introduction of carbon-containing modifiers causes predominant formation of filmy, planar , planar-veil nanostructures (fig. 1 c.) with a thickness of 10-50 nm.

Piezoeffect of quartz (Saito R. 1998, Biisenbaev M.A. 2004, Mansurov Z.A. 2006, Biisenbaev M.A. ) is considered as a constituent part of modification process of the surface of particles with organic compounds. Decomposition of piezoelectric is accompanied, as it is known [11], by exoelectron emission in the order of hundreds of kiloelectron - volts that substantially accelerates modification process.

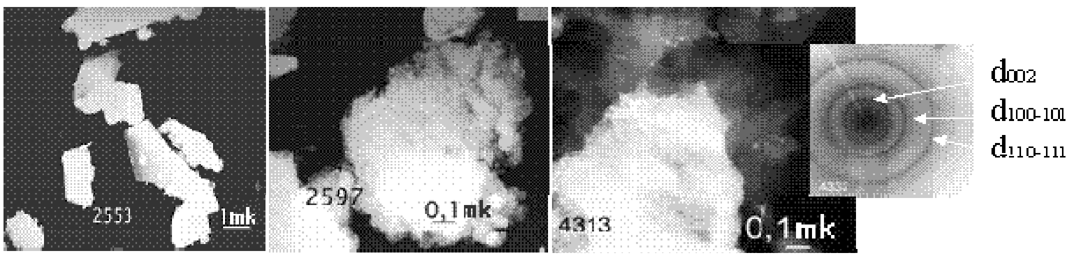



**Figure 1.** Electron-microscopic images: morphology of quartz particles in initial (a), activated (b) and modified (c) states. Microdiffraction pattern of the synthesized carbon filmy formation on modified particle.

Chemical reactions under action of electric field stimulates self-organization of nanostructurized composite systems. Obvious confirmation of that serves experimental results on modifying quartz particles with involving nitrogen-containing compounds (Abdulkarimova R.G. 2006), particularly, ammonia ($NH_4OH$). There were discovered crystallites which have "energy moiré effect" (fig. 2).

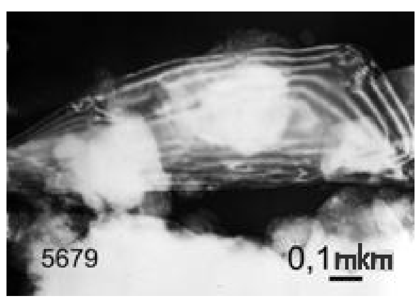
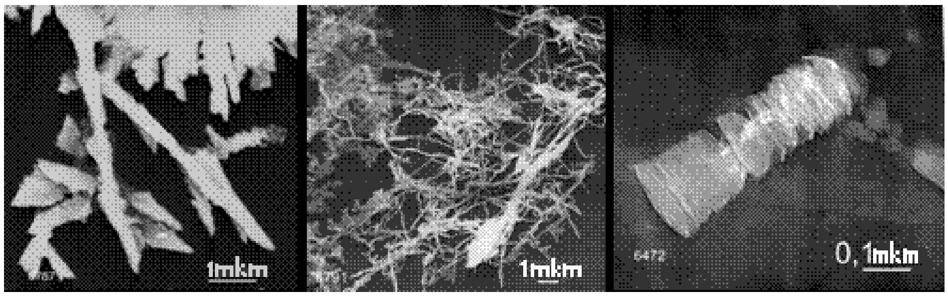



**Figure 2.** Elecron-microscopic image of quartz particle modified by ammonia ($NH_4OH$).

Stable fixation of these structures is conditioned by interaction of the surface of quartz particle with nitrogen-containing modifier. Thus, in the process of mechanochemical treatment of quartz with different additives multi-staged process of forming new structures on particle surface occurs as a result of grafting to radical centers ($\equiv Si^{\bullet}$ и $\equiv SiO^{\bullet}$) emerging on the surface of the split of the groups of decomposed compounds – modifiers.

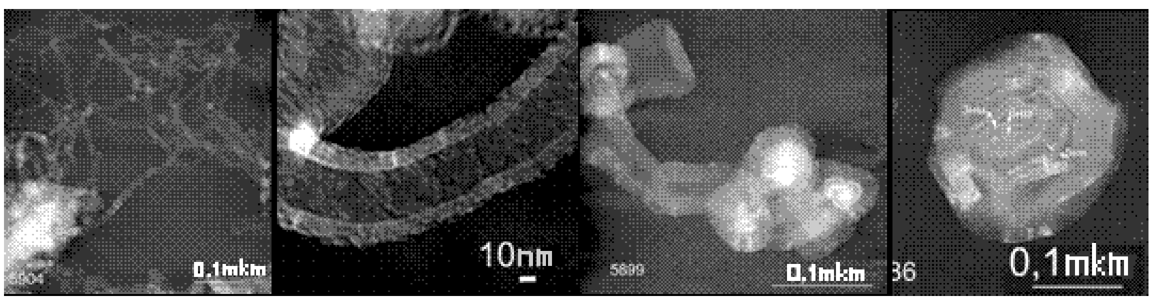
***2. Synthesis using carbonization***

Synthesis of nanostructurized materials is carried out by carbonization. Initial aluminosilicate base (zeolite) was carbonized in revolving quartz reactor, in the flow of carbon gas at the predetermined temperature (Biisenbaev M.A. 2005). Flexibility of the process allows creating a number of materials possessing necessary structural characteristics. Variation of metal – catalyst, chemical and concentration composition of gas environment and temperature regime of the process is possible. Substances obtained in different regimes contain different species of carbon nanoparticles (Mansurov Z.A. 2007). Among them there are: carbon-containing skeleton (fig. 3a), and wire (fig. 3b) crystallites; different carbon conic composed of many plates (fig. 3c), single-layer (fig. 4a), multi-layer nanotubes (fig. 4b); compact graphite nanotubes (fig. 4c) and "graphite roses" (fig. 4d); several species of tubular-filar (with periodically visible internal channel) particles (fig. 5).




a b c

**Figure 3.** Electron-microscopic images of particles: skeleton (a), wire (b), conic tubular composed of many plates (c).




a b c d

**Figure 4.** Electron-microscopic images of synthesized particles: single-layer (a), multi-layer (b), compact (c) nanotubes and "graphite rose" (d).

Some of them lamellar ones have winding or "ragged" walls. Besides, presence of predominant orientation of bulges formed on the walls of the tubes of last species stipulates their possible facet pattern (fig. 5a). Tubular-petal systems composed of separate links are rounded formations (fig. 5b).

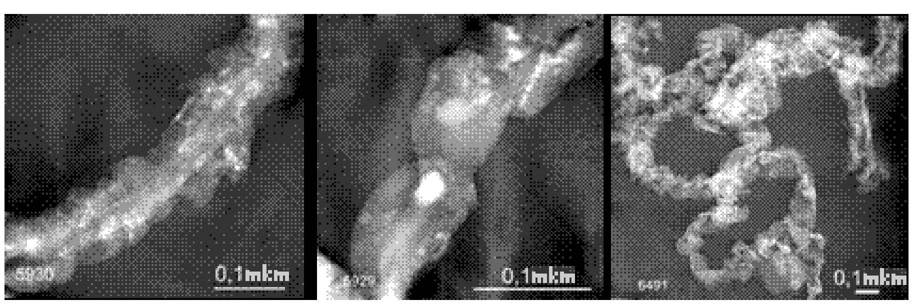



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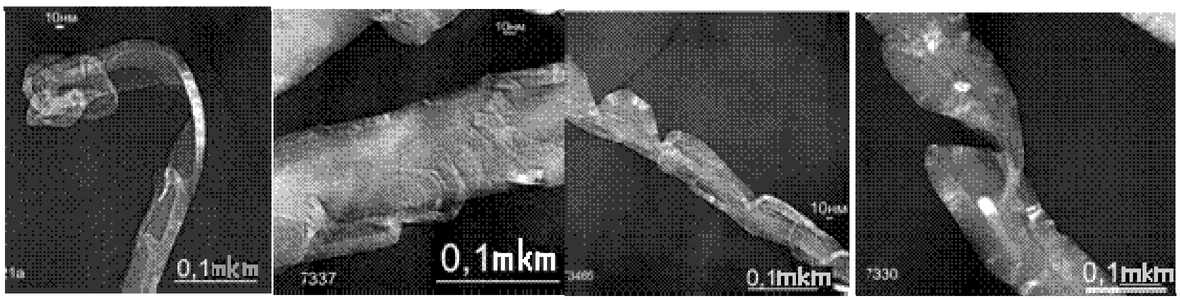
**Figure 5.** Electron-microscopic images of synthesized particles: lamellar (a), tubular – petal (b), petal-filar (c).

Figure 5 shows tubular-petal particles with a complex structure of walls. Practically, all of the indicated species of the particles can form large aggregates. Materials consisting of these formations have high specific surface and sorption capacity.

**3.** ***Hybrid method***

The facts given above initiate the work on creating silicon-carbon materials by two indicated methods. Samples of natural quartz were subjected to mechanochemcial treatment in centrifugal – planetary mill. Then, activated silicon dioxide which contains metal inclusions was undergone carbonization in quartz reactor in the flow of carbon gas at the temperature of 750 $^{o}$ C. Material obtained during experiment along with already known seven morphological structures of nanoparticles (Shabanova T.A. 2004), contains novel – two species of ribbon structures. The first one are large particles -ribbons (fig. 6a) usually have facet pattern. Their sizes are: in length to 1 mkm, in width about 80 nm and in thickness about 10 nm. They are often rolled in rounded formations – "graphite roses". It should be noted that "graphite roses" were discovered by us and described earlier but only in this experiment there was gained a proof that they are formed during rolling ribbon structures. Particles – ribbons can split into: separate planes, stitch structures (fig. 6a) and layers which are similar to the layers of puff paste (fig. 6 b arrow). Thickness of these layers is from 2 to 10 nm.




a b c d

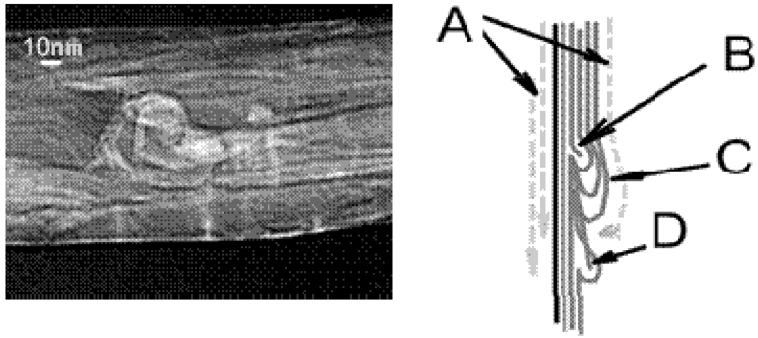
**Figure 6.** Electron-microscopic images of nanoparticle surfaces. The rolling of ribbon particle and formation of stitch structures on its facet pattern (a). Formation of layers reminding layers of puff paste (b). Multi-layer stitch structures; disclosure of metal-containing multi-layer carbon bud (d).

The second species – small ribbons, rolled in stitches. The thickness of a layer forming a stitch is 1,3 nm. Stitches are usually composed of two layers (about 5-8 nm) and packs composed of three and more layers are met more rarely. Multi-layer (3 and more layers) stitches usually have clearly expressed external and weakly discernable internal layers but, exactly, internal layers often give a rise to formation of new stitches (fig. 7a). Peripheral part of particles composed of tightly packed stitch formations is usually multi-layer. Structural ordering of carbonaceous substance in this zone is close to graphite one.

Formation of stitches can be explained by presence of swirling inhomogenities in the field of flow of carbon gas flowing around growing tube and supplying to it "building material" providing stage character of forming similar structures.

Inhomogenities being observed can appear because of presence of defect on the growing surface, for example, lamination showed in the figures 6 a, b or 7a. Further – according to Ostwald's rule: pressure above bulged part of a sample is always higher than above even surface. Instability, being formed, creates whirling pressure drops that leads to emerging stitch structures. Speed of substance condensation in the wave of increased pressure is obviously higher than condensation speed of defetless part of the surface of lamellar particle (tube, thread). Data obtained by us don't contradict to the experiments on growth of nanoparticles in zones of periodical instability conducted earlier.

Presence of metal-containing inclusions causes formation of laminated capsule. According to steam-liquid-crystalline and carbide mechanisms during cooling metal carbide which is inside "bud" there is occurred rejection of struturized carbon with forming additional internal capsulating layer (fig. 6d). Heat of metal phase (carbonisation temperature of 750 $^{o}$ C) causes break of carbon capsule and emission of the part of material. Constantly coming carbon stimulates continuation of the growth of tubular-filar phase and formation of new capsule around metal phase and stitch structures from defects containing on the surface of particle. In our opinion, morphological structure in the fig. 7 is a good illustration of the proposed "explosive" mechanism.




a b

**Figure 7.** Morphology (a) and scheme of formation of ribbon structures (b). A- - flow of carbon gas; B – layer defect; C – carbon layers being formed; D – curving carbon layer (secondary defect).

## Conclusion

Experiment on synthesis of silicon-carbon nanocomposite with methods of mechanical activation and subsequent carbonisation in the flow of carbon gas allowed discovering novel structural type – carbon stitches. Tubular-filar formations containing such structures should posses unusual electric and magnetic properties which periodically repeat within particle. Besides, special creation of similar structures on the surfaces of nanoparticles will allow using them as marks or elements of fixing system of construction materials.

On the basis of theories of growth of nanoparticles and numerous experimental data we proposed a possible mechanism of formation of stitch structures.

As follows from the data given above magnetic properties of the materials synthesized by the indicated methods will have different nature.

## References

Abdulkarimova R.G., Ermekova Zh.S., Mofa N.N., Ketegenov T.A., Mansurov Z.A. 22-24 June 2006. Alumino- and coal-thermal combustion of silicon dioxide modified by nitrogen-containing compounds. Pages 134-137. *Proceedings of IV International Symposium "Physics and chemistry of carbon materials / Nano engineering.* Almaty, Kazakhstan.

Biisenbaev M.A. 14-16 September 2004. Formation of carbon during pyrolysis of hydrocarbons in magnetic field. Pages 141-143. *Proceedings of III International Symposium "Physics and chemistry of carbon materials / Nano engineering.* Almaty, Kazakhstan.

Biisenbaev M.A. Nurmukhambetov N.N., Tazhkenov G.K., Seitimbetova G.K., Mansurova R.M. 2005 Study of carbon-mineral sorbents based on mineral raw materials. *KazNU Vestnik, chemical series – 204*. 4 (36) : 426-430

Buchachenko A.L. 2003. Nanochemistry – direct way to high technologies of new century. *Uspekhi Khimii* 5 (72) : 419-437.

Gibbs D.B. 1982. Thermodynamics. Statistical mechanics. *Nauka* p. 217, Moscow.

Gubin S.P., Kozinkin A.V., Afanasiev M.I., Popova N.A., Sever O.V., Shuvaev A.T., Tzirlin A.M. 1999. Clusters in polymer matrix. III. Composition and structure of Fe-containing nanoparticles in ceramic – forming silicon-organic polymers. *Inorganic materials*. 2 (35) : 237-243.

Lyakishev N.P., Alymov M.I., Dobatkin S.V. 2002. Nanomaterials of constructive use. *Conversion in mechanical engineering.* 6 : 125-139. Moscow.

Mansurov Z.A., Mofa N.N., So D. 3-5 Oktober 2006. Perspectives of synthesis of nanostructurized composite materials of special use. Pages 534-543. *Proceedings of International Conference "Metallurgy XXI – condition and strategy of development"*. Almaty, Kazakhstan.

Mansurov Z.A., Shabanova T.A., Maruf Khegazi, Biisenbaev M.A., Mofa N.N., Mansurova R.M. 2007. Morphological structures of nanoparticles of different chemical processes. *KazNU Vestnik, chemical series.* 1(45) : 384-389.

Molchanov V.I., Yusupov T.S. 1981. Physical and chemical properties. *Nedra*. 170. Moscow.

Saito R., Dresselhaus G., Dresselhaus M.S. 1998. Physical Properties of Carbon Nanotubes, London. *Imperial Press College*. 358.

Nassenshtein Kh. 1962. Electronic emission from surface of solids after mechanical treatment and radiation in Collection: Exoelectronic emission under ed. of Kobozev N.I., translation – Krylova I.V. *Inostrannaya literatura.*72-95. Moscow

Tretyakov Yu. D., Lukashin A.V., Eliseev A.A. 2004. Synthesis of functional nanocomposites based on solid-phase nanoreactors. *Uspekhi Khimii*. 9 (73) : 975-997.

Shabanova T.A., Tazhkenova G.K., Nurmukhambetova N.N., Mansurova R.M. 2004. Morphology of micro- and nanoparticles of carbonised mineral raw materials. *KazNU Vestnik, chemical series.* 2 (34) : 135-141.