SYNTHESIS OF POWDERLIKE MATERIALS WITH PARTICLES ENCAPSULATED IN NANOSTRUCTURIZED CARBON CONTAINING FILMS

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Introduction

At present great attention is paid to creation of nanostructurized materials, the properties of which considerably differ from those of course grain analogues. When obtaining powderlike nanosystems, the material may be not only a homogeneous ultradisperse powder but also nanolayer formations of a micrometer size. Creation of such microcomposition formations with nanosize morphology of constituents is one of the perspective directions with the designed complex of properties. When obtaining such composition nanomaterials, carbon- and silicon containing systems are paid special attention due to the peculiarities of their properties and a wide range of applications. Surface nanostructures play a significant role in such objects as highly disperse adsorbents, catalysts, filling agents of composition materials as well as in the materials for electronic industry. Mechanochemical synthesis has great advantages compared to other methods in the production of highly disperse nanostructural matherials. In the process of intensive dispersion of particles in dynamic mills, a chemical interaction between the substances being ground takes place. With the appropriate choice of the regime of mechanical effect on the powderlike mixture of a definite composition it is possible to synthesize particles with the layer change of the phase composition, structure and properties.

As it was shown [1-3], 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 subseguent application. The obtained magnetodielectric powders contain a dielectric material as a carrying nucleus, in particular quartz, on the surface of which one or several layers of compounds with the thickness of 10-50nm with magnetic, electric and other properties are synthesized. The properties of the material being produced depend on additives-modifiiers and conditions of the mechanochemical effect. The most effective modifiers are different carbon containing compounds providing the formation of nanosized compounds on the surface and encapsulating a quartz particle into films of different structures and density.

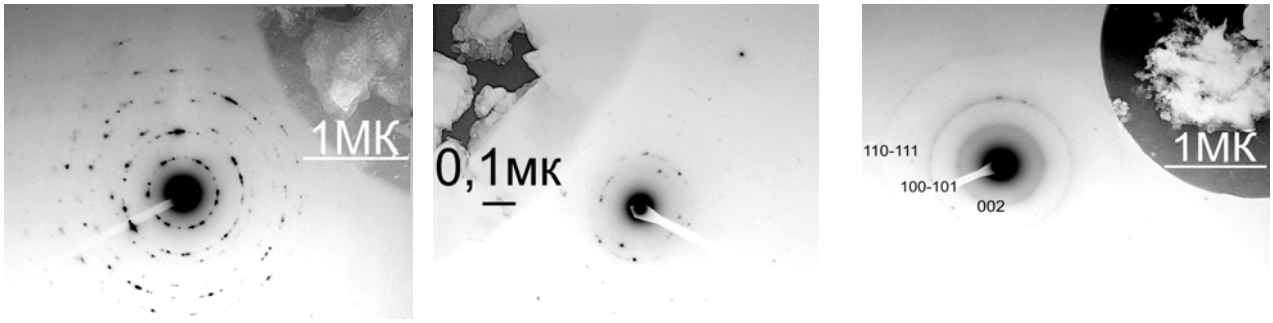
Experimental

For mechanochemical synthesis quartz with the purity of 99,8% was taken and carbon containing compounds (alcohols,polymers and their mixtures) were used as modifiers. Dispersion of quartz was carried out in a mill of centrifugal-planetary type (mechanical reactor). The time of treatment varied from 5 to 30 and more minutes.

The obtained material was studied by the methods of X-ray phase and electron microscopic analyses. Besides, the methods of IR-, EPR- and Messbauer spectroscopy were used. The sequence of structural rearrangement of surface carbon containing layers of quartz particles depending on the modifier and the conditions of mechanochemical treatment was analyzed. Measurements of induced ferromagnetism and electrical resistance of quartz at different stages of structural changes of the system were made.

Results and Discussion

The structure of the modified quartz particle and its transformation in the process of mechanochemical treatment is vividly shown by the results of electron microscopic investigations. After grinding in the mill without modifying organic additives, the surface layer of the particle becomes partially amorphized and the ultradisperse iron being ground is introduced into the surface from the walls of the milling vessel and balls. These structural changes were analyzed in detail in [1-3]. The main volume part of such particles remain crystalline, this fact being verified by the results of electron microdiffraction (Fig.1a). When using a dispersing organic additive to the quartz being ground in a centrifugal-planetary mill, the structure of particles undergo considerable changes. The surface layer is a dense or porous multiplayer formation of a different structure. The pictures of electron microdiffraction show the process of transformation of quartz particles (Fig.1a). into a composition material containing particles with partially amorphized and modified structure (Fig.1b) up to the formation of dense carbonaceons structures on the quartz surface (Fig.1c).

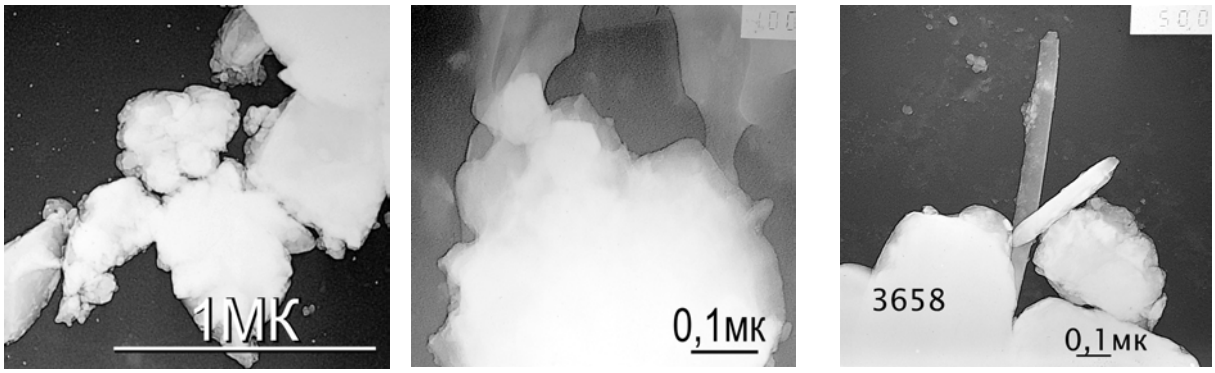


a b c

Fig.1. Electron microscopic pictures and electron diffraction of modified particles quartz.

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
Films, fiber or nanotubes (Fig.2a-c) are formed on the surface depending on the kind of the carbon containing modifier being used (alcohols, polystyrene) and the time of

treatment. After mechanochemical treatment, particles of quartz do become encapsulated in a layer film with the thickness of 10-50 nm strongly bound with the surface of the particle. According to the results of IR-, EPR and Messbauer spectroscopy, the composition and the structure of this coating include carbon and iron. According to the results of IR- spectroscopy, Si-OH, Si-O-Si, Si-O-C, Si-CH_3, C=O and C=C groups are the components of the structure of the surface layer modified by organic compounds of quartz.



a b c

Fig.2. Electron microscopic pictures at different stages of formation of a modified layer of a quartz particle.

The observed structural forms are in conformity with the known notions on soot formation depending on the raw material being used [3,4]. When using alcohols, i.e. polyene additives, structure formation of the modified quartz surface proceeds by “the acetylene way” when the most stable structures of carbon clusters up to C_{20} are chains and cycles. This is verified by the presence of transparent degree of carbonization in the samples as well as the formation of dense carbon films on the surface of quartz. When modifying quartz with polystyrene, one may observe a great variety of different structures, as a polystyrene molecule contains a polyene and aromatic constituent of the structure. Under the effect of mechanochemical treatment the destruction of a polymer chain with the formation of polyenes and aromatic fragments takes place. As a result, “carbonization” of the quartz particle surface proceeds by the scheme of coagulation of large polycyclic aromatic molecules, i.e. according to the “aromatic” hypothesis with simultaneous participation of polyene compounds. In electron microscopic pictures it is indicated by the variety of modified structures. The characteristic peculiarity of the process is the formation and growth of carbon nanotubes on the particle surface. Ultradisperse iron introduced into the surface of quartz particles catalyzes their growth.

The obtained results on structural investigations of modified quartz particles are in good agreement with the experimental data presented in [4]. So, in different systems, in particular silicon containing ones, apart from point defects, there are structural macrodefects in the form of clusters-small local aggregations of Si atoms and SiO_2 molecules and other adsorbed molecules, chemical groups with local concentrations considerably exceeding average values all along the area. The

mentioned nanosize in homogeneities noticeably influence electro physical and other characteristics of the structures formed.

Thus, 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. The values of magnetic permeability and specific resistance change depending of the kind of the modifying additive and he time of treatment (Table 1).

Tabl 1. –The change of specific resistance and magnetic permeability of quartz powder depending on the time of weathering. Grinding was carried out during 5 minutes.

Material	Specific resistance, $\rho\ 10^{6}$,Om m		Magnetic permeability	
	The time of weathering, τ_{st}, 24 hours		The time of weathering, τ_{st}, 24 hours	
	0	30	0	30
Quartz	1,1	6	2,0	2,0
Quartz +butanol	6,0	15,0	4,0	3,2
Quartz + polystyrene	2,5	3,5	29.0	27,0

Both electric and magnetic characteristics of mechanochemically 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.

Conclusion

Quartz was stated to undergo considerable changes after a mechanochemical treatment in a centrifugal –planetary mill in the presence of different organic additives. The obtained powder material exhibits conducting and magnetic properties. The observed transformation of properties is due to the formation of new compounds in the surface layers of particles. The results of spectroscopic and electron microscopic investigations of quartz particles modified by carbon containing compounds show the peculiarities of rearrangements of the surface structure depending on the kind of organic modifiers. In some cases, the presence of

nanoparticles of metallic iron and its compounds with silicon in the organic film encapsulating the particle as well as the presence and growth of carbon nanotubes were detected. The formation and growth of carbon structures in the form of films and tubes on the surface of quartz particles indicate the consequence of transformation processes of the modified quartz structure when mechanochemicaly treated.

References

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