Quartz Particles Electron-Microscopic Investigations Modified by Mechanochemical Processing

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Abstract

There were taken and analyzed electron-microscopic images of quartz particles after mechanochemical processing in mill-activator with different organic modifiers. It was stated that quartz surface suffers serious changes the peculiarities of which are defined by used modifiers. Quartz particle has a complex flaky morphology. Friable surface layers represent as carbonic element-organic formations with ferrous additives. The change of particle's surface layers are responsible to modified quartz physicochemical properties transfer.

Introduction

In the works published before [1-3] we have shown that quartz properties after the mechanochemical processing in planetary-centrifugal mill with different organic additives undergo substantial changes. Produced powder becomes a good sorbing matter, besides, it shows conducting properties and magnetizing abilities. These properties transformations are caused by the changes of defect structure both in the volume and on the surface of the particle, and also new compounds are formed in the surface layers. These compounds are the result of the reaction centers interaction on the edges of the quartz particle crack and organic additives, being coupled into disperse medium and iron grated from the surface of milling containers and balls. In the result of mechanochemical processing we have quartz powder particles with modified surfaces.

According to the results of infrared spectroscopy [4] when as the modifying additives alcohol (one, two, three atomic), active carbon, polysterene, silicon and acrylic acids are used the structure of modified quartz surface is represented as the following groups: Si-OH, Si-OC, Si-C, C=H_2, C=OH and C=C. Because of that implanted organic matter concentration is low and lays in the interval < 1200 and 3000-3800 cm^{-1}, a strong absorption from the main matter – quartz – takes place, infrared spectrums allow to say that only few organic groups exist on the surface. It is quite difficult to make any conclusion about implanted groups conformation basing only on the infrared spectrum. The only real thing we can conclude is that in the surface layer structure a major role belongs to the carbon in his various mixtures with silicon and organic elements. So, when quartz is being mechanically processed with presence of organic additives on the surface of dispersed quartz particle carbon and it's compounds stratification takes place. To have more full insight about modifying layers structure we need a systematical research of the synthesized powder matter using various methods. The electronic microscopy method gives us a good opportunity, first, to define changes in shape of the solid particles after the implantation on to their surfaces different organic complexes under mechanochemical processing and analyze the structure of the surface layers.

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Experimental

In the recent article the results of electronic-microscopic research of the quartz particles after various conditions of the mechanochemical processing with different modifying additives (alcohol butil, active carbon, polysterene) are represented. The investigation was held on the electronic translucent microscope "Jem-100CX", U – 100 kV. The specimens were prepared by the suspension in distilled water with following ultrasound dispersing. In the process of investigation it became clear that water interacts

with the alcohol remaining left after quartz abrading; silicon acid – the result of this interaction – changes a morphology and structure of the specimen and using ultrasound destroying the structure of the specimen, also brings to the changes in polymeric properties of the implanting high polimeric compounds. Because of that the following specimen preparations were hold dry.

Results and discussion

As the primary not modified quartz mountain crystal particles, prepared were researched abraded in agate vessel with no dispersing medium, *i.e.* "dryly". Such quartz particles are shown on the Fig.1. A medium size of the particle is about 2 μm, but larger ones – 8-10 μm – and smaller ones (0.5 μm) occur (Fig. 1a). Particles usually have sharp edges. As we work with natural samples they may contain different micro additives.

Using a dispersing medium (alcohol) in quartz hand abrading in agate vessel with agate pestle favours not only to the gaining a higher disperse powder, and also brings to the organic matter sorption by defect structure of being comminuted particles. X-ray structure analysis doesn't feel these changes, because in the means of amount they lay in the area of method's mistake and roentgenogram shows narrow sharp reflexes of the crystal quartz (Fig. 2a). However, while preparing suspense for the researches on the electronic microscope a silicon acid formed, which lead to a melting process of not only the surface, but also the inner quartz crystal structure (Fig. 1b). It was displayed in almost complete reflexes collapse on the micro diffraction image. Using an ultrasound on dispersing this specimen in the suspense preparing process brought out carbonic lamina, a gross of which was probably lead from ultrasound action (Figs. 1c, 1d).

Represented results of electron-microscopic researches on quartz, comminuted in agate stamp in presence of alcohol, firstly show that specimen preparing must not be a sort of water suspense and no ultrasound action must be held. The particles seen in the microscope give no information about a matter being investigated, because it suffers magnificent changes in the researching object preparing process. Because of that all the following researches were held on specimen prepared by dry preparation method.

The particles of the quartz dispersed in planetary-

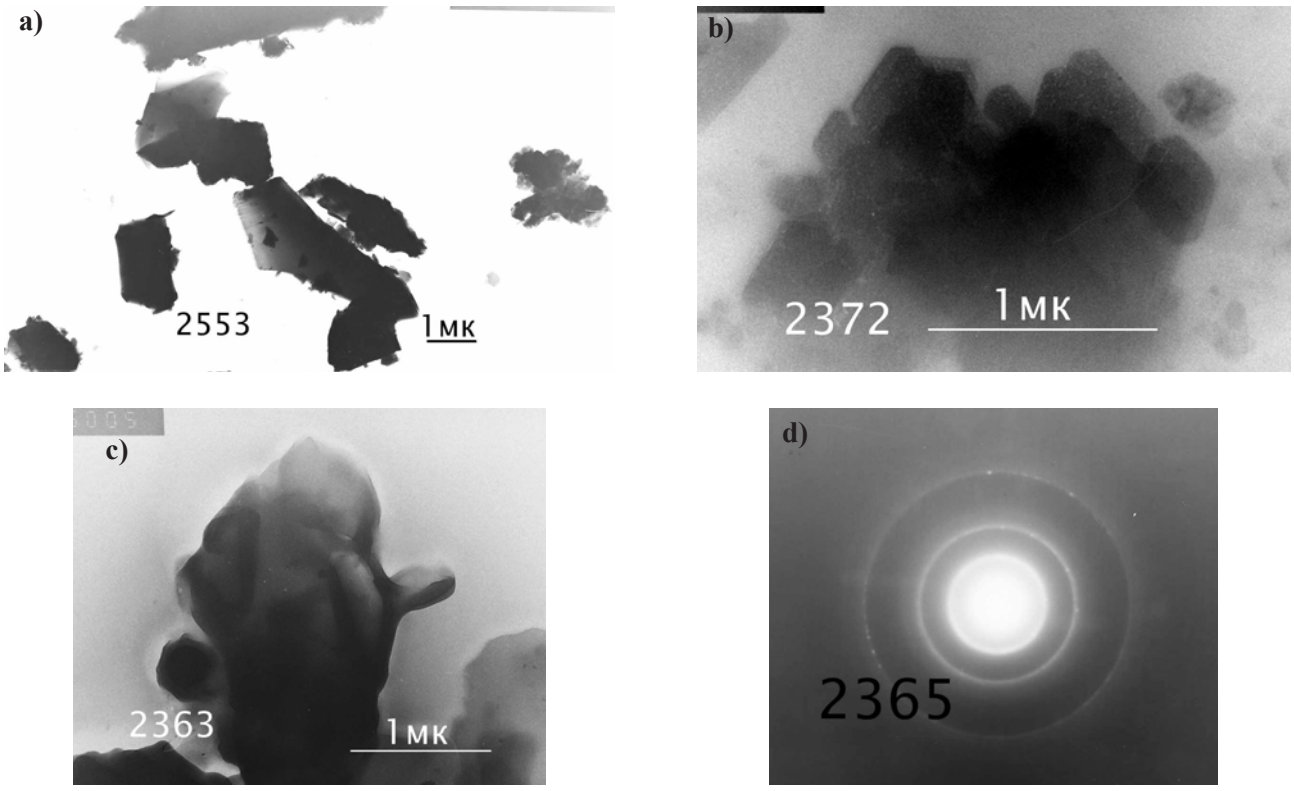


Fig. 1. Quartz electron-microscopic images after dry abrading in agate vessel (a) and in the presence of alcohol (b, c); a picture of carbonic substance diffraction on the quartz specimen abraded in alcohol (d) (1 мк = 1 μk).

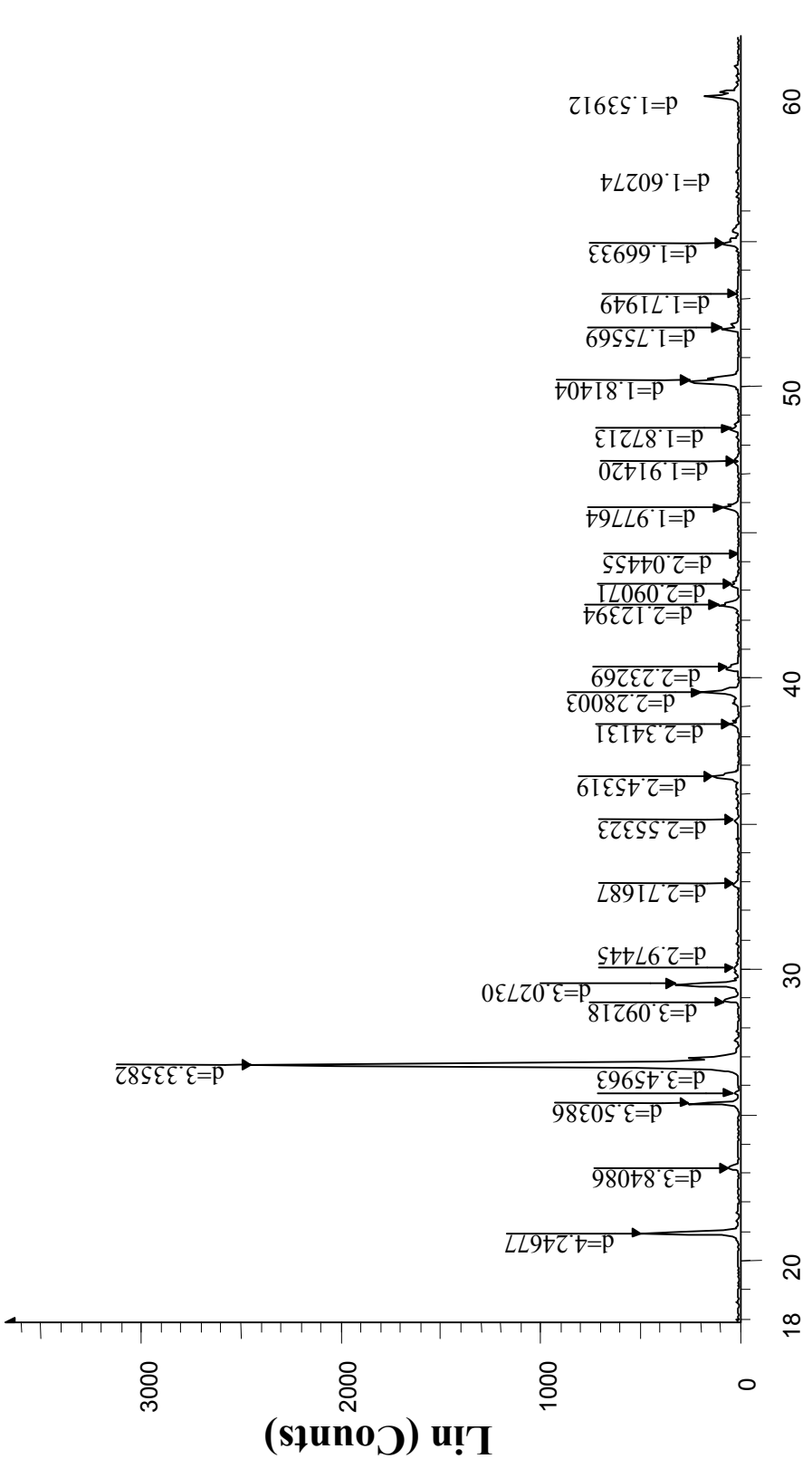
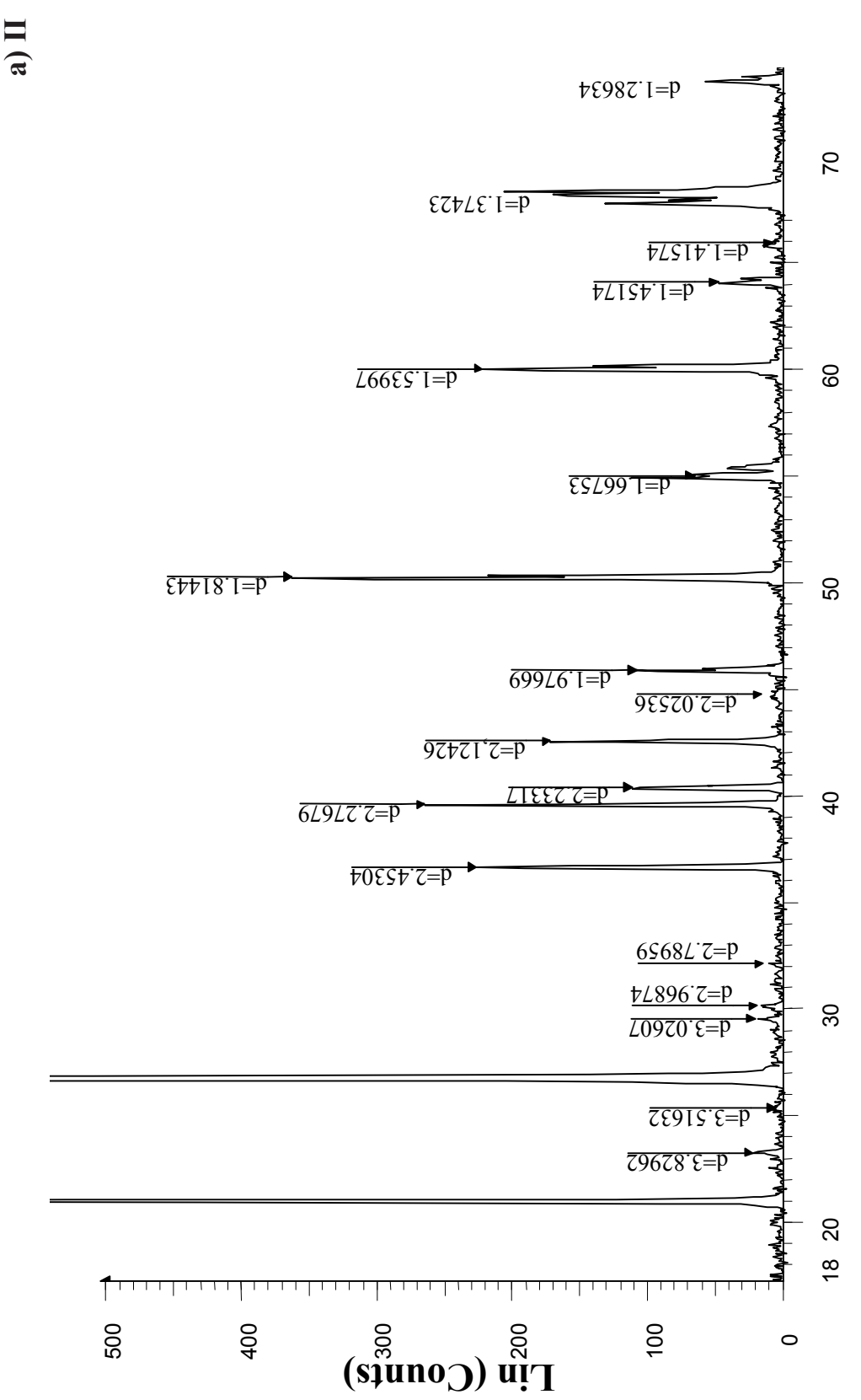


Fig. 2. A roentgenogram (a) of starting quartz (I) and dispersed in planetary-centrifugal mill (II). Electron-microscopic image (b) of quartz particle abraded in mill.



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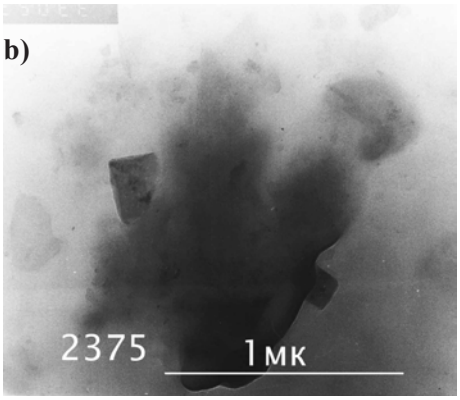

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centrifugal mill (steel containers with steel balls) are shown on the Fig. 2b. In the process of thrashing chafing and implanting iron containing compounds onto the quartz particle surface (Fig. 2a). These areas are shown as more intimate generations on the surface of particles with sizes 0.3-0.5 μm (Fig. 2b).

When butanol is used as the dispersing addition to quartz abraded in planetary-centrifugal mill its particles suffer serious changes. With a part of high dispersible powder (particles are about 0.02 μm) dense crystals occur (1-2 μm) with sharp seen edges in the comparison with quartz hand abraded (Fig. 3a). Besides, there is seen a friable and flaky structure of the particle surface (Fig. 3b, 3c) in which we can observe more dense additives (Fig. 3b, 3d).

According to the results of X-ray phase analysis, EPMR and Messbawer spectroscopy [1,5], these additives contain a metallic iron or represent a $Fe(SiO_2)$ compounds. For separate particles (Fig. 3e) in boundary layers we observe a complex inner structure with denser compounding parts (0.01 μm) in these surface formations.

This way, quartz processed with butyl alcohol in amount of 5% to the weight of dispersed matter represents a heterogenic mixture of powder containing quartz particles with sharp edges and clear surface. Also there are particles with complex enough surface structure consisting various elements which is represented as organic formation covering particles and containing metal additives. Decoding these structures is a separate problem. When polysterene is used (as a carbonic polymer) as an additive to the dispersing quartz with the particularities listed above there are compounds in the particles structure analogous to the nanostructural carbon compounds. Surfaces or rolled laminas have been fixed (Fig. 4a) which occur over forming and developing of carbon nanotubes [6]. Existence of directivity (textured surface) of carbonaceus particles in membranous formations that is proved by micro-diffraction images (Fig. 4b).

A structure of quartz particle surface layer can be interpreted as a containing element-organic forma-

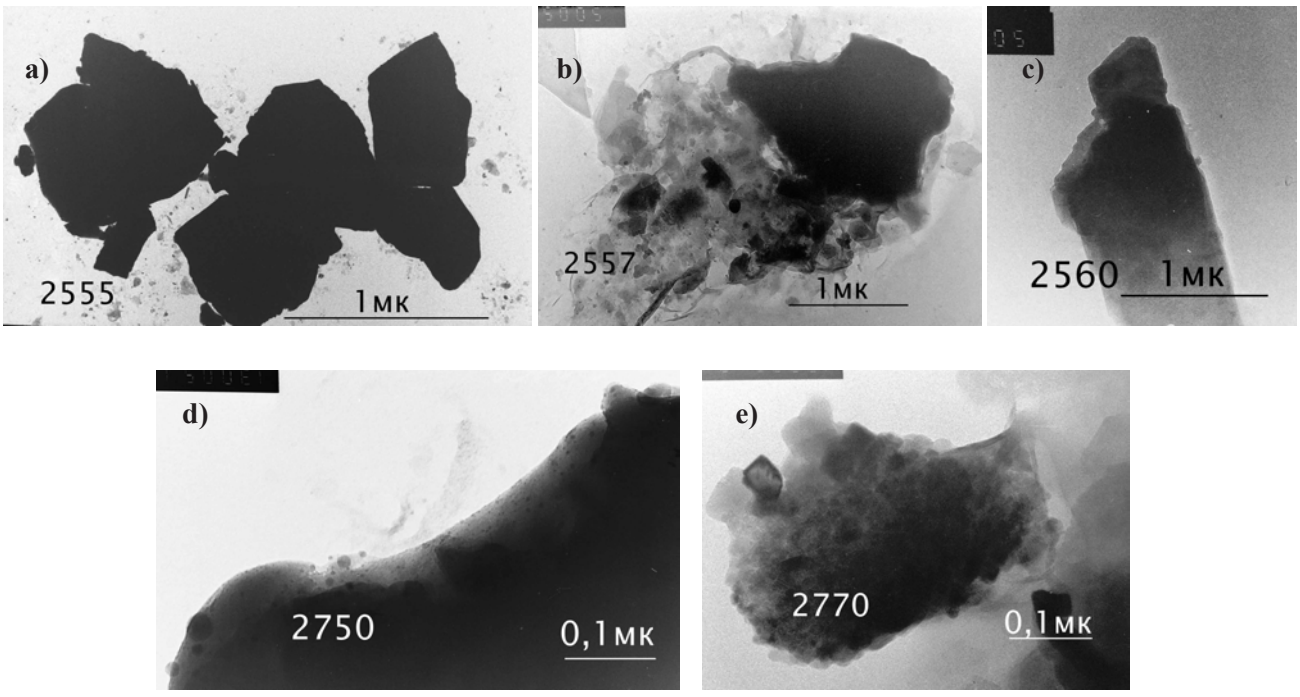

Fig. 3. Electron-microscopic pictures of quartz powder particles dispersed in planetary-centrifugal mill with butyl alcohol.

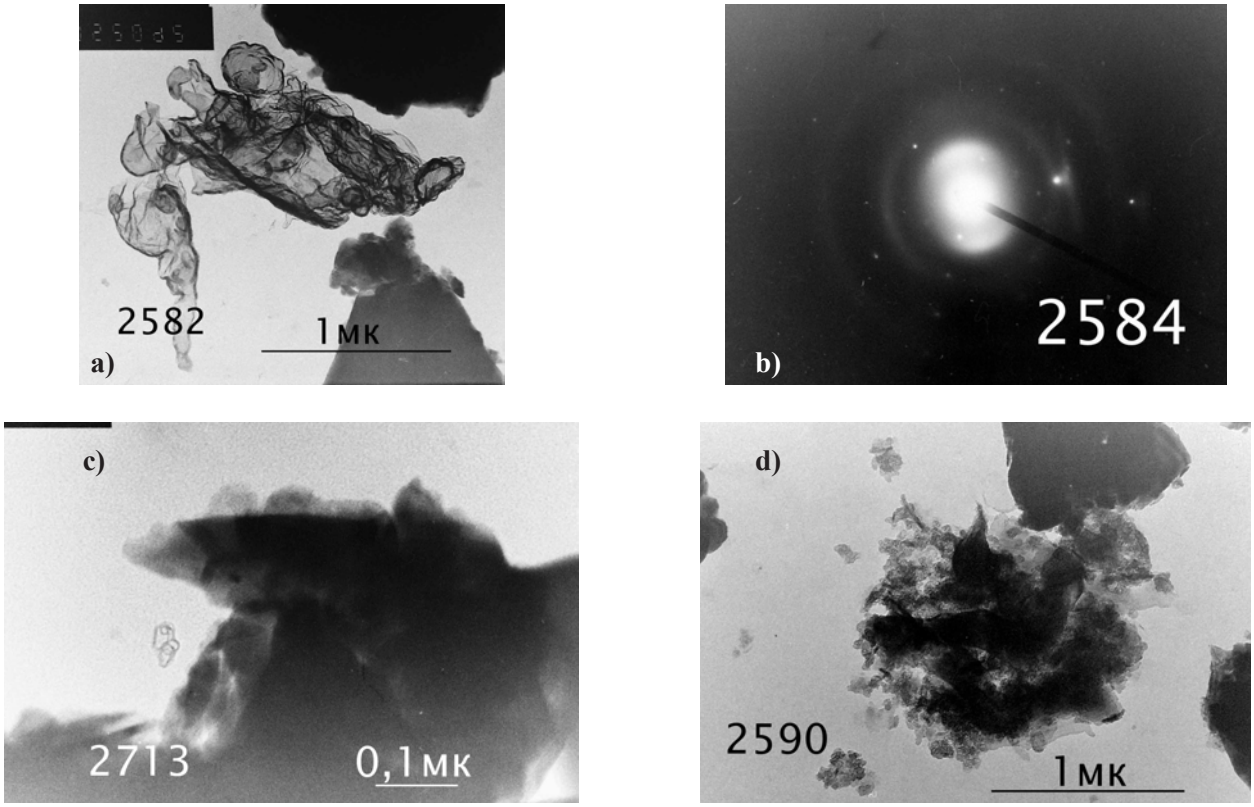

Fig. 4. Quartz electron-microscopic images (a, c, d) and electronogramm (b) dispersed in planetary-centrifugal mill with 5% polysterene.

tions and a lamina covering particle's surface (Figs. 4c, 4d). The structure of these laminas has a complex enough morphology, various thickness and density. Almost all particles are captured into element-organic formations where dense iron additives enter, too.

When active carbon is used as a modifying addition a set of distinctive peculiarities appear. The surface becomes more mellow – amorphous (Fig. 5a). We can clearly observe areas with hardened carbon structure on the particle edges and metal additives (Fig. 5b). At the same time we often observe not separate particles, but a conglomeration of bound together particles with various sizes and shapes.

In the same way, quartz particles electron-microscopic researches modified by mechanochemical processing showed visually a complex structure which changes seemingly dependently to the used modifier. However, in all cases we deal with predominantly flaky morphology of particles which have friable enough surface layer the structure of which we may interpret as a polymeric element organic formation with high disperse (~10 nm) iron containing additions. Such surface formations could relate to "claspols" [7]. This fact supports a conclusion we made above while researching magnetic properties of quartz powder with surface modified by mechanochemical processing [5].

A fact of organic additive interaction with quartz surface under mechanic action was visually enough demonstrated on initial stages of our work with powder suspense dispersed by ultra sound action.

On one hand this stage of the work showed an inadmissibility of this method, on the other hand it had visually demonstrated us interaction process of absorbed on the quartz surface alcohol with active centers which extra appear under ultra high sound action.

A formation and gross of carbon lamina on quartz surface shows an image of whole structure conversion processes of modified quartz taking place in the dynamic action mill. A formation of carbonic compounds on the surface of dispersed particle goes through active centers ($\equiv Si^*$ and $\equiv SiO^*$) appearing on the quartz fracture surface according to all laws pointed in the review of V.A. Radcig [8]. Observed quartz particles structure transformation dispersed in the presence of organic substances corresponds to known conceptions [9] about a possibility of holding triggered by various methods, also by mecha-

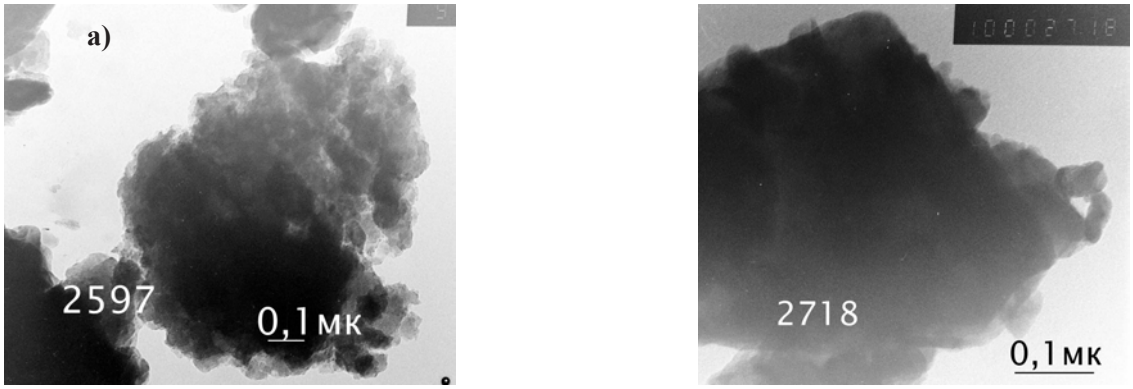

Fig. 5. Quartz electron-microscopic images dispersed in planetary-centrifugal mill with 5 % carbon.

nochemical processes, polymeric reactions on solid surface.

Conclusions

This way, electron-microscopic snapshots visually demonstrated the existence of modified structure on quartz particles surfaces after mechanochemical processing of the matter. A difference in quartz surface morphology is found in the dependence from used organic additive modifiers. Heterogeneity of modified particles surface is discovered. The particularities of quartz structure modified by mechanochemical processing execute the specificity of physical and chemical properties of this matter being observed.

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