Magnetism of Nanocomposite Quartz Powder by use of MCR Method

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Abstract— **The materials showing high structure dispersion with functional properties were developed on the quartz base and those were obtained by mechano-chemical reaction technology. Depending on the processing conditions and subsequent applications the materials produced by mechano-chemical reaction show concurrently magnetic, dielectric and electrical properties. The obtained magnetic-electrical powders classified by aggregate complex of their features as segnetomagnetics, containing a dielectric material as a carrying nucleus, particularly the quartz on that surface one or more layers of different compounds were synthesized having thickness up to 10~50 nm showing magnetic, electrical properties and others. The similarity of the structure of surface layers of quartz particles subjected to mechano-chemical processing and nano-structure *cluspol (clusters in a polymer matrics)* material was also confirmed by the fact that the characteristics of ferromagnetic quartz of insulating nano-composite powder were changed with time, after its preparing process was completed. The magnetic permeability of the sample was decreasing within first two months down by 15~20 %. Then, the magnetic characteristics were almost stabilized steadily and continuously. The observed changes were related with defective structure of the particles, elastic stress relief, and changes of electron density and magnetic moment in deformation zones. This process of stabilization of the investigated properties could be intensified by the thermal annealing heat treatment in short time period of the nano-composite quartz powders at the temperature ranges of 100~150 °C.**

Keywords : magnetism, quartz, mechano-chemical reaction, segnetomagnetics, nano-composite powder

I. INTRODUCTION

The composite materials showing concurrently dielectric and magnetic properties have now found their particular place in microelectronics aimed at developing proven memory and storage devices as well as to creating different transducers, modulators and electromagnetic spin and acoustic spin wave generators. Such materials are classified as segnetomagnetics. The reversibility of polarization in electromagnetic field; reversibility of magnetization in magnetic field; double optical refraction (natural and modulated) and absorption; dependence of resonance frequencies of spin waves on the applied magnetic field and stable operation within millimetric and IR bandwidth are the most important factors determining their applications.

One of the most-promising and effective ways in developing of segnetomagnetic materials having required properties is a targeted synthesis of solid solutions and production of materials showing nano-composite structures of surface layers. The above mentioned surface layers could be performed in certain stratified sequences of crystalline, amorphous or organo-metallic structures having different properties varying in a very wide range including electrical, dielectric, magnetic and many other properties depending on the special applications of such materials.

II. Experimental

The mechano-chemical synthesis was applied to obtaining such powder composites when concurrently intensive dispersion of particles in dynamic highly powered mills of the chemical reactions was proceeding between substances subjected to milling. The synthesis is applied to obtaining such powder composites and concurrently to intensive dispersion of particles in dynamic highly powered mills. When dispersing quartz in the mill of centrifugal-planetary type (Fig. 1) with the platform rotation speed of 700 revolutions per minute and that of grinding vessels equal to 1200 revolutions per minute with participation of different alcohols and iron chloride as a modifier, we have obtained quartz powder with ferromagnetic properties. A considerable decrease of its specific electric resistance was also stated.

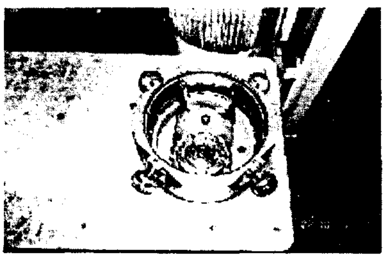

Fig. 1. Photograph of the centrifugal-planetary type mill.

Specially selected conditions of mechanical processing of powder mixtures having predetermined compositions will result in obtaining particles showing layer-by-layer changes in phase compositions, structures and properties. The potentialities of mechano-chemical synthesis applications are limitless, making possible to obtaining materials with divers combinations of structures and properties across the particles notable for their high dispersion, including particles classified as segnetomagnetics. The materials showing high structure dispersivity were investigated and developed on the quartz base, which were obtained by mechano-chemical reaction technology. Depending on the processing conditions and subsequent applications, the materials above mentioned show concurrently magnetic, dielectric and electrical properties. The obtained material was analyzed by methods of x-ray phase, x-ray spectral and electron microscopic analysis as well as IR, and Mëssbauer spectroscopy.

III. Results and Discussion

The obtained magnetic-electrical powders contain a dielectric material as a carrying nucleus, particularly the quartz on that surface one or more layers of different compounds were synthesized having thickness up to 10-50 nm and showing magnetic, electrical and other properties. Such materials are classified by aggregate complex of their features as segnetomagnetics. The synthesis of surface layers of quartz particles was proceeding with involvement of different organic compounds and halogenides in reaction, including the salts of transition metals. The properties of obtained materials are determined by used modifying additions and by conditions of mechano-chemical processing. So, in process of quartz dispersion in centrifuge-planetary mills at platform rotation rates up to 700 rpm, and rotation rates of milling vessels up to 1200 rpm, using different alcohols and iron chloride as modifying agents, a quartz powder was produced showing ferromagnetic properties. The synthesized materials were investigated with IR, EPR and Mëssbauer spectroscopy methods. The induced ferromagnetism of quartz was determined by variations of relatively efficient index of magnetic permeability (μ) of the powder compacted into the tablets of 1.4-1.5 g/cm^3 density. The quartz ferro-magnetism was registered after five minutes of each sample processing [1].

Fig. 2 presents the investigation results obtained for changes in quartz magnetic permeability with processing time duration. With extension of processing time from 5 minutes to 30 minutes the magnetic powder permeability was changed increasingly on the curves from 2 to 4. With 5 % alcohol (ethanol) addition to the reaction mixture (2), the quartz magnetic permeability increased from 4 to 12 during 30 minutes of milling process. In presence of butanol addition (3) known as effective modifying agent of the surface of particles subjected to dispersion, the magnetic permeability of investigated material was also increased within 30 minutes of processing.

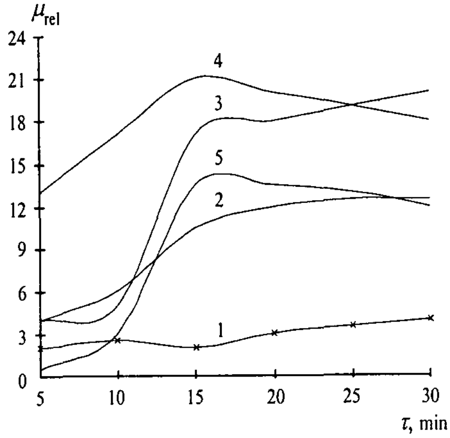

Fig. 2. Dependence of magnetic permeability on the activation time in mechano-chemical reaction processing; (1) quartz without additions, (2) quartz with additions of 5 % ethanol, (3) buthanol, (4) ethyleneglycol, (5) 15 % iron chloride

The use of bibasic alcohol, ethyleneglycol (4) as organic addition was resulted in showing of ferro-magnetic properties by quartz even after 5 minutes of material processing.

Its magnetic permeability increased to 13 just after only 5 minutes processing. After more prolonged exposure to processing (over 15 minutes), the magnetic permeability was increased up to 21. Then a certain decrease of value was determined down to 17 gradually. With use of iron chloride (5) as a modifying agent, the magnetic permeability of treated quartz did not exceed 14.

The results of spectral methods of analysis confirmed the fact that ferromagnetism of quartz after mechano-chemical treatment is caused by the formation of an ordered imperfect structure and iron-containing clusters in a polymer matrix on the surface of particles being dispersed in the presence of alcohols (ethanol, butanol, ethyleneglycol) and iron chloride. X-ray phase and X-ray spectral analyses showed the presence of both free and bound iron in quartz. As grinding of quartz was carried out in steel vessels and with steel balls, iron got into the material being dispersed, thus contribution to the development of magnetic properties of the powder. Depending on the conditions of mechano-chemical treatment (time, the number of balls, type and amount of modifiers) the iron contents in quartz changes (table 1).

In initial quartz the amount of iron admixtures was 0.1 weight %, after a thirty-minute grinding at the ratio M_p/M_b=1/4 it was 5.36 weight %. After grinding in the presence of modifiers, the iron content of quartz under the same conditions of grinding increased 2-3 times. The presence of iron in quartz after mechano-chemical treatment is a significant but in sufficient factor for

Table 1. The iron content according to the results of X-ray spectral analysis before and after etching of modified quartz.

Material	The iron content after mechano-chemical treatment, %	The iron content after cold etching of modified quartz, %	The iron content after hot etching of modified quartz, %
Quartz	3,02	0,69	0,06
Quartz+butanol	14,85	11,18	0,56

development of magnetic properties in the dispersed material. There is no proportional dependence between the iron content and the value of magnetic permeability of the modified quartz.

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It was known [2] that the magnetically ordered state of deformed particles was determined by formation of defective structure consisting of charged hole centers with formation of collective spin. In this connection a significant role was attributed to the structure of surface layers and those formations were mainly determined by alcohol additions. In conditions of intensive mechanical processing (high local temperatures and pressure) a destruction of organic compounds and their interactions with active deforming centers were occurred on the surface of quartz particles [3].

Therefore, this mechanical processing resulted in modification of particle surface with inoculation of organic complexes on the silicic ion (=Si*) and siloxane (=SiOSi=) reaction centers. So, in case of using alcohol for example, there are hydroxyl and methoxyl groups in organic complexes. The presence of transition metal ions contributes to polymerization of a solid surface resulting in the formation of metal polymer formations [4]. It is known [5] that in the process of mechanochemical polymerization both grafted and non-grafted polymers (homopolymers) are formed considerably differing in structure.

The results of spectral analysis methods confirmed that the ferromagnetism of the quartz subjected to mechano-chemical processing was resulted by formation of ordered defective structure and iron-containing clusters in polymer matrix on the surface of the particles to be dispersed in presence of alcohols (ethanol, butanol, ethyleneglycol) and iron chloride. The presence of the polymer grafted to the particle surface and non-grafted homopolymer between particles was well illustrated by electronic microscopic pictures of quartz modified particles (Fig. 3).

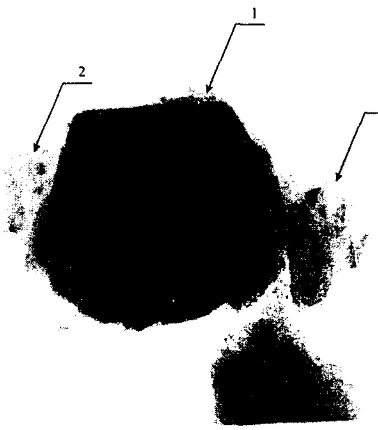

Fig. 3. Electron microscopic picture of quartz modified nanocomposite particle polymerized (x 400,000);
(1) polymer grafted to the particle surface,
(2) polymer non-grafted (homopolymer)

The surface is supposed to be represented metal complexes in a polymer matrix. The metal complexes were included with Fe, FeSi, FeC, etc. The obtained experimental results also confirmed the possibility of capsulating the mechanically treated solid quartz particles into the metal-polymer nano-structure sheath showing magnetic properties, for example of *cluspol* type, which was named from *clusters in a polymer matrix* [6]. The metal-polymers of *cluspol* type were the polymer matrices with metal clusters in the cavity. They had unique electrical, physical and magnetic properties of wide range applications, which would be determined by multiphase structure of metal nanoparticles interacting with polymer matrices.

IV. Conclusion

The similarity of the structure of surface layers on the quartz particles subjected to mechano-chemical processing and nano-structure *cluspol* materials was confirmed by the fact that the characteristics of ferromagnetic quartz were changed with time, after its processing was completed. It is known that such *cluspols* may develop magnetic and electro-conducting properties, a wide spectrum of which was determined by a multiphase structure of metal nano-particles interacting with a polymer matrix.

The values of relative magnetic permeability of the modified quartz ferro-magnetic nano-composite materials were in the range of 10 to 20, after 20 minutes of reaction processing in presence of alcohols and iron chloride. However, the magnetic permeability of the samples was decreasing within first two months in period down by 15-20 %, as an aging effect, and then, steadily stabilized.

The observed changes were related with defective structure of the particles, elastic stress relief, and changes in electron density and magnetic moment of deformation zones. This process of stabilization of the investigated properties could be intensified by the annealing treatment of the powders at the temperature range of 100-150 °C in short period.

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