Nanocomposite Magnetic Powder Materials using Mechano-chemical Synthesis

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The materials showing high structure dispersity have been developed on the quartz base by mechano-chemical technology. Depending on the processing conditions and subsequent applications, the materials produced by mechano-chemical reaction (MCR) showed concurrently magnetic, dielectric and electrical properties. The obtained magnetic-electrical powders classified by aggregate complex of their features as segneto-magnetics, contained a dielectric material as a carrying nucleus, particularly the quartz on that surface one or more layers of different compounds was synthesized having thickness up to 10~50 nm and showing magnetic properties and etc.

Keywords : Quartz, Magnetic property , Dielectric material, Segneto-magnetics, Mechano-chemical reaction (MCR)

1. INTRODUCTION

The composite materials showing concurrent dielectric and magnetic properties have now found their particular position in microelectronics aimed at developing proven memory and storage devices as well as to creating different transducers, modulators, or electromagnetic spin and acoustic spin wave generators. Such materials belong to the class of magneto-electrics and are classified as segneto-magnetics. 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 the stable operation within milli-metric and IR bandwidth, are the most important factors for their applications[1]. One of the most promising and effective ways in developing segneto-magnetic materials having required properties is a targeted synthesis of solid solutions and production of materials showing nano-composite structures in the surface layers[2,3].

The above mentioned layers may be performed in certain stratified sequences of crystalline, amorphous or organo-metallic structures having different properties, varied in a very wide range including electrical, dielectric, the magnetic and many other properties depending on the special applications of such materials. The obtained magneto-dielectric powders have a dielectric material as a carrying nucleus, in particular, quartz on the surface of which one or several layers of compounds were synthesized with the thickness of 10-50 nm of their magnetic, electric and other properties. These materials belong to the class of segneto-magnetics by a number of indexes combined.

2. EXPERIMENT

Synthesis of surface layers of quarts particles was taken place with participation of different organic compounds and halogens including transition metal salts. The properties of the material being prepared were determined by additives-modificators and conditions of mechano-chemical effects. The mechano-chemical synthesis was applied to obtaining such powder composites and concurrently to intensive dispersion of particles in dynamic highly powered mills. When it was done to dispersing quartz in the mill of centrifugal-planetary type with the rotating speed of platform 700 rpm and that of grinding vessels equal to 1200 rpm with participation of different alcohols and metal chloride as a modifier, we cloud obtained the quartz powder with ferromagnetic properties. A considerable decrease of its specific electric resistance was also stated.

The chemical reactions were proceeding between substances subjected to milling. The mechanical processing conditions selected specially for powder mixtures of predetermined composition would result in layer-by-layer changes of particles in phase compositions, structure, and properties. The potentialities of mechano-chemical synthesis applications are unlimited and making it possible to obtaining materials with divers combinations of structures and properties across the particles. The obtained material was analyzed by the methods of x-ray phase, x-ray spectral and electron microscopic analysis as well as IR, and Mössbauer spectroscopy. The formed ferromagnetism of quartz was evaluated by the change of relative "effective" index of magnetic permeability (μ) of the powder compacted in a tablet with density of 1.4-1.5 g/cm^3. Quartz ferro-magnetism was fixed after five minutes treatment[4].

The electric resistance of the ground quartz was measured on the sifted out fraction of powder with the particle sizes less than 60 μm pressed in ample to the density of (3.7-4.0) 10^{-3} g/mm^3.

3. RESULTS AND DISCUSSION

The results of resistivity measurement showed its decrease after quartz grinding by over an order. The longer the grinding is the lower the resistance of quartz powder (Fig.1).

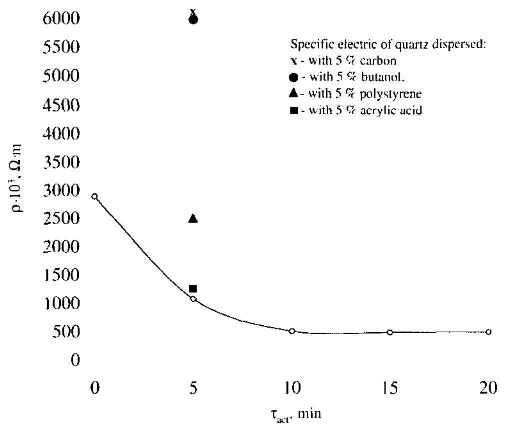

Fig. 1. Resistivity variation of quartz depending on time of mechanical treatment.

The introduction of 5% modifying additives (carbon, butanol, ethanol, ethylene glycol, polystyrene, acrylic and silicon acids) into quartz during grinding resulted in different changes of specific electric resistance of dispersed quartz. Quartz treated with alcohols and silicon acid remains to be a dielectric with a higher specific resistance than in its initial state. The use of polystyrene and acrylic acid contributes to the decrease of electric resistance of quartz powder. The results of measuring electric resistance of quartz treated with carbon (graphite) deserve special attention and will be considered separately in the following article.

On the whole, it follows from the results obtained that the structure of quartz and particularly the particle surface layers undergo significant changes after mechano-chemical treatment. The materials become electric. After such treatment it is in a meta-stable state. The resistivity on the modified quartz powder changed, at first decreasing (in case when conducting properties were improved after mechanic effect) during the first 2-3 days and then increasing to the level of resistivity of underground quartz (Table 1). The obtained results indicate the fact that in the materials there were taken place of relaxation post processes due to disproportional change of imperfect structure, relaxation of elastic stress, recombination of radicals in the surface layer, and decrease of surface charge. The change of specific electric resistance of quartz treated in the presence of other modifiers (alcohols, acids, polymers) had a tendency to grow up, but with different intensity. For the quartz modified by polystyrene or acrylic acid, this process was slow. Thus mechanical treatment (dispersion) in the presence of carbon containing modified additives resulted in deep changes of internal state and structure of a substance. These changes were such that, after mechano-chemical treatment quartz exhibits not only electro-conducting properties but also magnetic ones.

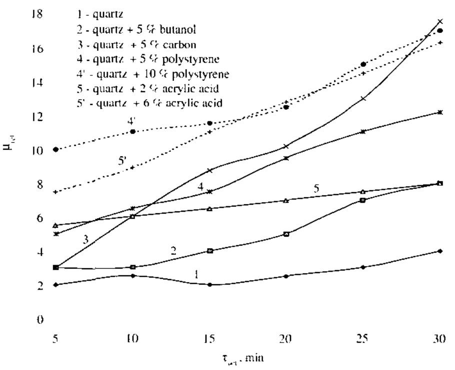

Fig. 2. Dependency of effective magnetic permeability of quartz on the time of mechano-chemical treatment with modifying additives.

Table 1. The change of specific electric resistance of quartz powder with weathering time after grinding with different modifiers.

Material	Time of grinding, τ_{act}, min	Specific electric resistance ρ (x 10^6 Ω·m)		
		The time of weathering, τ_{ct}, days		
		0	7	21
Quartz		3.0	3.0	3.0
Quartz+5% butanol	5	1.1	1.4	5.0
Quartz+5% butanol	5	6.0	10.0	12.0
Quartz+5% polystyrene	5	2.5	2.7	3.2
Quartz+5% acrylic acid	5	1.2	1.7	2.3

Table 2. The change of magnetic permeability (μ) of quartz with the mechanical treatment time (τ_{act}) and weathering (τ_a) after mechano-chemical activation with different modified additives.

Material	Grinding time τ_{act}, min	Ageing Time τ_a, months			
		0	2	12	18
Quartz	5	2.0	2.0	1.5	1.5
	20	3.5	3.0	3.0	2.5
Quartz+5% butanol	5	4.0	3.5	3.0	1.5
	20	17.0	15.0	5.0	3.5
Quartz+5% polystyrene	5	29.0	29.0	2.5	24.5
	20	32.0	31.5	30.5	30.0
Quartz+5% acrylic acid	5	14.0	14.0	13.0	13.0
	20	17.0	16.7	16.0	15.0

Figure 2 shows the dependency of magnetic permeability of quartz on the time of activation, type and amount of modifying additives. With the increase of time mechanical treatment from 5 to 30 minutes magnetic permeability of quartz changes within μ = 2 - 4.

Treatment of quartz in the presence of butanol for 30 minutes increased the μ up to 7. The use of carbon as a modifier contributed to magnetization of quartz up to μ = 15. Quartz modified by polystyrene and acrylic acid at the amount of 4-5 % showed the change of magnetic permeability with the time of activation within 5 to 11. With the increase of the modifier amount to 6-10 %, magnetic permeability of the material increases to 8-18 % with the time of treatment from 5 to 30 minutes. The further increase of the modifier amount was not expedient because magnetic properties of the material were not intensified. The ratio of the mass of powder/ grinding balls (M_p/M_b) plays more significant part for increasing magnetization of quartz in the course of mechano-chemical treatment. With the ratio of these indexes 1:4, magnetization of quartz increased considerably (Fig.3) in both of the electric and magnetic characteristics of mechano-chemically treated quartz with time. A gradual decrease of magnetic permeability of powder was caused with the time of weathering i.e the material "ages" (Table2).

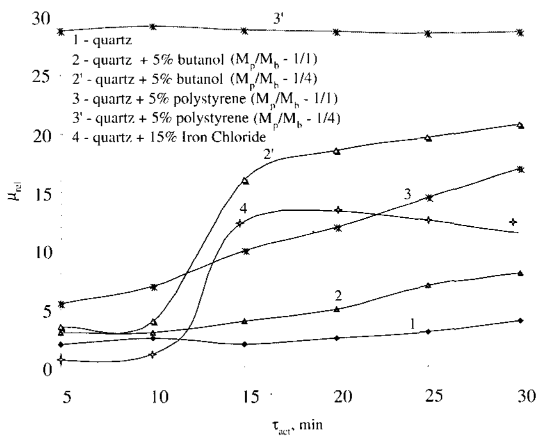

Fig. 3. Dependency of magnetic permeability on the time of mechano-chemical treatment of quartz with modifying additives at different ratio of powder mass and balls.

Table 3. The iron content according to the results of X-ray spectral analysis before and after etching of modified quartz.

Material	Iron content after mechano-chemical treatment, %	Iron content after cold etching of modified quartz, %	Iron content after hot etching of modified quartz, %
Quartz	3.02	0.69	0.06
Quartz + butanol	14.85	11.18	0.56
Quartz + carbon	14.60	2.25	1.26
Quartz + polystyrene	11.2	2.5	1.32

According to the data given in the table, for quartz which had been ground for 20 minutes at the ratio of M_P:M_b =1:4 the changes of magnetic permeability as a result of natural ageing were not more then 10-15%. When modifiers were used, magnetization of quartz increased in the course of mechanical treatment and the ageing effect became more expressed (the decrease of μ from 20 to 75%). However, for the quartz modified by polystyrene and acrylic acid, both electric and magnetic properties get stabilized. Ageing was expressed in a lesser extent for them. It is known [5] that magnetically ordered state of deformed particles was determined by the formation of imperfect structure with charged hole center of the formation of a collective spin. A significant part was played here by the structure of surface layers in the formation of which alcohol additives played a determining role. Under the conditions of intensive mechanical effect (high local temperatures and pressure), destruction of organic compounds and their interactions with active deformation centers on the surface of a quartz particle was taken place[6]. As a result there was placed modification of the surface of particle grafted on silicon (Si) and siloxane (SiOSi) reaction centers of organic complexes. For example, using alcohols these were hydroxyl and methoxyl groups. The presence of transition metal ions contributes to polymerization of a solid surface resulting in the formation of metal polymer formations[7].

It is known[8] that in the process of mechano-chemical polymerization both grafted and non-grafted polymers were differently formed in structure. The peculiarities of the grafted polymer structure were determined by the structure of the support, type, amount and distribution of reaction centers on which cross-linking of the polymer with inorganic nucleus took place in the course of particle dispersion.

The results of spectral methods of analysis confirmed the fact that ferromagnetism of quartz after mechano-chemical treatment was 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, ethylene glycol), polystyrene, acrylic acid and iron chloride. X-ray phase and X-ray spectral analysis 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 was taken place. 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 3). 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 was a significant but in sufficient factor for development of magnetic properties in the dispersed material. There was no proportional dependence between the iron content and the value of magnetic permeability of the modified quartz. The greatest content of iron was found to be in quartz treated in the presence of acrylic acid, and maximum magnetization was that of the powder with carbon and polystyrene. After etching the powder in hydrochloric acid the amount of iron decreased, but differently defending on the organic modifier used. Hence, iron was present in quartz powder both in free and bound state. Unbound iron was dissolved by hydrochloric acid. Parts of it were shielded by polymer formations grafted to the particle surface and inaccessible for acid effect. Shielding of iron on quartz particles modified by carbon and polystyrene was more effective. When boiling powder was in acid, polymers were destructed and iron-containing clusters interact with the acid. And only iron chemically bound with quartz surface in the form of $FeSi_2$ compounds remains chemically stable. To analyze the structure of the surface layer of the modified quartz particle, IR-spectroscopy of the obtained material was carried out. The results showed that the distinctive peculiarity of the modified quartz was the presence of adsorption bounds of Si-O-H, Si-O-C, C-O-H, C=O, Si=C. These adsorption spectra were characteristics of all modified samples. The difference was only in intensity of bonds. When using acrylic acid as a modifier, absorption bounds of C=O, O-H, C=C, C-H, C-H_2 are also observed. Generality of IR spectra patterns for all kinds of quartz exhibiting different electric and magnetic properties speaks about the fact that IR spectra only reflect the structure of the cross-linking part clusters in the structure of surface polymer layers of modified quartz powder was confirmed by the results of EPR spectroscopy. It is a surface polymer layer white metal clusters that is responsible for long time conditions and magnetic properties of modified disperses quartz. This surface layer concentrated all iron, which was made up from 3 to 15 % by weight. The thickness of this layer does not exceed 1 mm. Then iron content of it will amount to 30 % by volume.

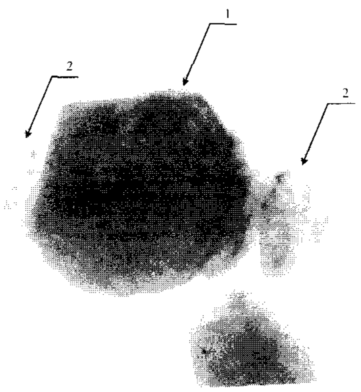

Fig. 4. Electronic microscopic picture of quartz modified particle (x 400,000). 1) polymer grafted to the particle surface, 2) homo-polymer.

The presence of the polymer grafted to the particle surface and homo-polymer between particles was well illustrated by electronic microscopic pictures of quartz modified particles (Fig.4). It could be supposed to be represented metal complexes in a polymer matrix on the surface. The metal complexes include Fe, FeSi, FeC, etc. It is known [9] that such "cluspols"-clusters in a polymer matrix may develop magnetic and electric conducting properties, a wide spectrum of which was determined by a multiphase structure of metal nano-particles interacting with a polymer matrix.

4. CONCLUSION

After a mechano-chemical modifying treatment, a quartz particle had a complex structure. It is capsulated into metal-polymer nano-structural shells of the "cluspol" type. The volume changes of the material and the structure of surface layers, the sizes of which do not exceed 100 nm determine property peculiarities of the powder material obtained by mechano-chemical synthesis on the basis of quartz. The structure analogy of surface layers of quartz particles after mechano-chemical treatment with nano-structural materials "cluspol" was also confirmed by the fact that characteristics of ferro-magnetic quartz changes with the time after treatment. Magnetic permeability of the samples became lowered to 15-20 % during the first two months. Then, characteristics got stabilized. The observed changes are due to the imperfect structure of particles, relaxation of elastic stress, changes of electron density and magnetic moment of deformation zones. This property stabilization process may be intensified by a short time annealing of the powder at 100-150°C. And magnetic properties after long time weathering "ageing" of the material were partially recovered when the powder was placed in an electromagnetic field.

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