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Mechanoemission and Related Phenomena – Electron-Hole Ferromagnetism in Nonmagnetic Dielectrics and Gas-Dusty Plasma. Possible Applications

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Abstract

Mechanoemission-related data obtained at the ISSCM SB RAS, and the most essential results from the literature are reviewed. The consequences of strong electron emission were recorded in the spectra of ferromagnetic and paramagnetic resonance at room temperature. Anisotropic noise-like spectra of ferromagnetic resonance with a signal-to-noise ratio of about 10^1–10^5 were observed after single acts of shock mechanical loading in a number of non-magnetic dielectrics, including NaF, KBr, NH_4I, TiO_2, $Al(OH)_3$, and others. Ferromagnetism is associated with the formation of metastable electron-hole states resulting from charge separation in slip planes under mechanical loading of powders. The relationship between intense mechanoemission of electrons and the formation of the dynamic state, namely dense aerosol of charged particles (gas dusty plasma), is highlighted. The features of a new class of eco-engineering facilities with the general name Electro Mass Classifier (EMC) based on the generation and relaxation of gas-dusty plasma are described. The results of model experiments on EMC showing the complexity of the ongoing processes but allowing one, to a certain extent, to predict trends, implement scaling and optimization of the technique are presented. The most promising areas of EMC application are listed, including the separation of dielectric powders, semiconductors and metals within a wide range of particle sizes ~10^{-1}–10^2 μm. In combination with planetary mills, EMC is used for nano-architectural design of composite materials. Effective removal of dust from fine natural and technogenic raw materials provides the possibility of dry selective separation.

Keywords: mechanoemission, mechanochemistry, ferromagnetic resonance, ESR, charged aerosols, separation of powders

INTRODUCTION

In 1982, Mechanochemical Centre was launched under the supervision of V. V. Boldyrev at the ISSCM SB RAS. The participation of the author of this paper in that process included both the development of the methodology of the fundamental development of mechanochemistry and the purchase of diverse necessary equipment.

At that time, the direction which is now related to mechanochemistry was dominated by mechanoemission, tribochemistry, mechanical alloying. The name of the scientific forum which was the most representative one in this area in the USSR was All-Union Symposium on Mechanoemission and Mechanochemistry of Solids, and this really depicted the state of this direction [1]. Since then, the situation has changed greatly: the interest of researchers to mechanochemistry itself is tens times higher than the interest to other close areas as suggested by the number of published papers.

Mechanoemission, as the scientific direction, started its intense development in 1953 after

B. V. Deryagin, N. A. Krotova and V. V. Karasev discovered mechanoemission of high-energy electrons from freshly formed surfaces in vacuum [1, 2]. The destruction of solids, film detachment, and generally the formation of defects in solids or deformation under the action of external or internal sources of strain are accompanied by the interrelated acoustic and electromagnetic (photons, radio waves) emission, the emission of charged (electrons, protons, ions) and neutral (in the normal and excited states) particles, including neutrons [1]. The peak of investigations was in the 1980-es but even at present the number of publications remains substantial, which is connected with the practical applications and progress in the area of emission detection. Emission of neutrons [1, 3] is the most interesting and scandalously famous phenomenon because of irreproducibility, which might be observed from nuclear transmutation even in biological systems [4].

The studies in mechanochemistry during those years were non-systematic, scattered, without a quantitative relationship between the parameters of mechanical load and the system response [5]. Various devices were used for mechanical treatment, and the strongest effects were observed in high-energy mills including planetary-centrifugal ones [6]. The treatment of solids in the steel environment was inevitably accompanied by powder contamination, which caused strong uncertainty for the interpretation of the observed phenomena. Because of this, the problem of obtaining fundamentally significant quantitative information on mechanochemical processes in pure samples was urgent, including the optimal choice or development of new devices for mechanochemical technologies.

EXPERIMENTAL

For fundamental quantitative studies, it was proposed to use the installations for single-act loads with the investigation of the response with the help of instrumental methods. Mechanical treatment of powdered samples was carried out using the installations of the types of impact machine (an imitator of impact) and a heavily loaded roller (an imitator of rolling) [7, 8]. The installations allowed one to provide the input of mechanical energy to the powders using different methods with the variations of velocity and magnitude. The amount of input specific energy for the installation was insignificant in comparison with mills, so a highly sensitive instrumental method was required to detect the response. The most suitable device for this purpose was radiospectrometer RE-1306, which was manufactured commercially in the USSR. Paramagnetic centres were often observed in various solids as a result of mechanical treatment [9]. Broadening of narrow lines in the EPR spectrum of Mn^{2+} in MgO was proposed as a test for mechanical action [10]. Investigation of the response revealed a rapid decrease in the input energy with the number of acts of mechanical loading. However, with loosening of the aggregated powder, nearly linear dependence of the response on the amount of input energy was achieved [10]. Thus obtained notions allowed developing a procedure of mechanical treatment of powders in planetary mills [11]. According to the procedure, the time of mechanical treatment in the apparatus, having no physical sense, is linearly connected with the input energy Periodic loosening of the material charged into the mill drum allows one to keep the powder agglomeration degree at a steady level and to bring the material from the dead zone in the corners of the cylinder back into treatment. Preliminary formation of stable lining composed of the material under treatment on the working surfaces of the steel milling environment and its conservation during the operation provided a decrease in the contamination of activated powders to a minimal level [12]. Optimization of the procedure allowed obtaining pure nanopowders even for abrasive materials with the Mohs hardness 8–9 [13]. The use of a correct procedure is the basis for obtaining quantitative data on the dynamics of ultra-rapid mechanochemical synthesis in oxide systems, which finally resulted in the development of a semi-quantitative theory of the process [14, 15].

RESULTS AND DISCUSSION

Mechanoemission and related phenomena in solids

The enormous effect of admixtures and impurities on mechanochemical processes, especially those related to emission, was discovered by us in [16] and analyzed in more detail in [8]. During mechanical treatment of high-purity anatase TiO_2 (Merck, Germany) in the AGO-2 planetary mill, three paramagnetic centres were discovered: a hole of O^- type and electron e^- and Ti^{3+}. The spectra of interstitial paramagnetic centres Ti^{3+}

with narrow lines at room temperature were discovered for the first time, and later on they were observed by other researchers (see references in [8]). During the mechanical treatment of anatase with a small (~0.01 %) content of admixtures of Fe^{3+}, Cr^{3+} type (Me^{3+}), the indicated paramagnetic centres were not observed, similarly to TiO_2 samples with rutile structure [16]. The most probable reactions in the system were described by equations [8]:

$$O^{2-} \rightarrow O^- + e^- \quad (1)$$

$$e^- + Ti^{4+} \rightarrow Ti^{3+} \quad (2)$$

$$e^- + Ti^{4+} \rightarrow Ti^{3+}_{is} \quad (3)$$

$$e^- + Me^{3+} \rightarrow Me^{2+} \quad (4)$$

$$e^- + [\ ] \rightarrow [e^-] \quad (5)$$

$$e^- + O^- \rightarrow O^{2-} \quad (6)$$

$$O^- + O^- \rightarrow O^{2-} + O^{\bullet}\uparrow \quad (7)$$

$$O^{\bullet} + O^{\bullet} \rightarrow O_2\uparrow \quad (8)$$

where reaction (1) is charge separation with the formation of holes and fast electrons, reactions (2)–(6) describe electron transformations with the charge exchange with matrix (Ti^{4+}, Ti^{3+}_{is}) and extrinsic Me^{3+} ions, capture in traps ([ ]) and inverse recombination, reactions (7), (8) relate to hole transformations. Some high-energy electrons with the energy of ~40 keV (according to [17]), similarly to ions, excited atoms and molecules, may leave the solid body, which had been reported by many researchers [1]. In [8, 16], attention had been paid for the first time to the necessity of the analysis of a balance between hole and electron centres formed as a result of charge separation in solids under external action. The deficit of hole centres was explained in [16] by the mechanolysis of TiO_2, that is, the reduction of titanium oxide by means of oxygen emission.

At the beginning of 1984, investigation of the response in the powder samples of a series of dielectrics of chemically pure and specially pure reagent grades treated with single acts in impact imitators had led to the discovery of unusual noise-like spectra of VHF energy absorption detected with the RE-1306 radiospectrometer (wavelength 3 cm, frequency 9.4 GHz) at room temperature [18]. The most intense spectra with the signal to noise ratio $I_s/I_n \sim 10^5$ were detected with NaF, KBr samples. In addition, similar spectra were observed with $I_s/I_n \sim 10^1–10^4$ for TiO_2 with the structure of anatase and rutile, ZrO_2, NH_4I, NH_4F, NaCl, KCl, KI, LiF, $Al(OH)_3$ and other non-magnetic dielectrics including quartz glass. Unusual spectra were observed in the case when energy input in one loading act was ~20 kJ/mol. Hammer mass was ~7 kg, and the spectra under consideration appeared only when the hammer was filled with lead pellets, which provided an impact without recoil and the time of powder load equal to $\sim 10^{-3}$ s. To prevent powder scattering, the impact was performed in forevacuum. For the indicated parameters of impact loading, the powder samples for spectrometry were tightly pressed discs that were semi-transparent in the case of NaF, KBr, NH_4I. As a rule, intense spectra were observed after three or four impacts, except for very plastic NH_4I (Mohs hardness 1), for which an intense spectrum was observed even after the first loading act. To perform subsequent loading acts, the discs were crushed into the pieces less than 1 mm in size, and placed onto a base shaped as a truncated cone about 5 mm high. To guarantee protection from contamination with magnetic materials, the samples were screened by protective foil made of titanium. A plate made of single crystal corundum or muscovite. The results observed in the spectra were identical. A substantial decrease in the intensity of the spectra after annealing of some samples (ZrO_2) for 6 min was observed only after the temperature of 300 °C was achieved. It became possible to explain the discovered phenomenon when the processes with charge separation and subsequent reactions during mechanical treatment of anatase in the mill were understood [16]. Experiments with pure substances under the conditions excluding contamination with foreign impurities allowed us to claim that electron-hole ferromagnetism was observed for the first time in non-magnetic dielectrics [18–21]. The first public presentation of the discovered phenomenon took place in the Laboratory of Radiospectroscopy of the Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, on November 15, 1985, with the seminar chairman S. P. Gabuda, Dr. Sci. in Physics and Mathematics, and seminar secretary E. G. Boguslavsky. All the specific features of the observed magnetic resonance spectra are listed below:

1. Very high amplitude of the envelope curve of noise-like spectra at $T \sim 300$ K.

2. Non-monotonous change of spectrum intensity, including oscillations with the number of loading acts after the achievement of the maximal intensity.

3. Very narrow lines: the typical width of inflections was ~1–10 G.

4. Pronounced anisotropy in the spectra of discs, depicting the plane of plastic deformation.

5. Observation of the lines within a broad range of magnetic fields ~1–4 kG.

All the known ferromagnetic dielectrics are characterized by Curie points T_C < 100 K and give broad lines in the spectra. Estimation of the number of spins in the samples with the most intense spectra on the basis of spectrometer sensitivity and the width of the envelope line gives the value about 0.1–1 mol. %. However, if we take into account the fact that the absorption VHF spectrum of the collective spin of ferromagnetics at room temperature is about 3 orders of magnitude more intense than that of the same number of individual spins in a paramagnetic because of different temperature dependence of the magnetization of ordered (3/2 Bloch law) and disordered (Curie law) spin states, the observed spectra are due to spin concentration 10^{-4}–10^{-3} mol. %. This concentration of paramagnetic centres arising during mechanical treatment does not contradict the published data [9].

Confirming the results with the help of an independent method, anatase sample treated with four impacts and exhibiting the high intensity of lines in the absorption spectrum was also investigated using a static method – magnetization measurement – at the Leningrad Polytechnical Institute by M. A. Kvantov, Cand. Sci in Physics and Mathematics (the data were reported in [8]). An expected result was obtained: a mixture of paramagnetic and ferromagnetic states with the typical dependence of magnetization on the magnetic field was observed in the sample. Measurements were carried out in a week after sample preparation, which is the evidence of a rather long lifetime of metastable electron-hole ferromagnetism. The plans of detailed studies into the kinetics of the sink of the ferromagnetic state as a result of the inverse reaction of recombination of electron and hole centres were outlined. For that purpose, an improved set-up was manufactured, and the basement for it was prepared at the Mechanochemical Centre in Academy Town. However, after the move from the city to the new building, the sensitivity of the spectrometer dropped by an order of magnitude, and scientific plans changed sharply in connection with the discovery of high-temperature superconductivity (HTSC). Nevertheless, some experiments had been carried out. The amplitude of signal envelope in the spectrum of NH_4I, sample treated with a single impact decreased by 2 % within 24 hours, and after storage for 3 months no spectra were observed. The sample got a characteristic colour due to the recombination of hole centres: $I^{\bullet} + I^{\bullet} = I_2$. Signal amplitude in NaF sample treated with four impacts decreased by 2 % after storage for 3 days in the resonator of the spectrometer.

The two-dimensional nature of ferromagnetic formations was confirmed independently by the observation of similar spectra in kaolin from the Angrenskoye deposit annealed at 500 °C [8, 22, 23]. Kaolin from that deposit is characterized by increased content (up to 2–3 mass %) of iron, which is not included into kaolinite structure but forms mixed-layer structures. Moreover, on the basis of the obtained results, in 1999 a joint work was carried out by researchers from the ISSCM SB RAS and IIC SB RAS: Search, investigation and development of radio-absorbing materials based on thermally stable polymeric matrices and fillers of various classes. Radio-absorbing material was clay shale of black colour containing a mineral close in structure to nontronite but with low iron content (~6 %). After special treatment, the fraction of 2D-ferromagnetic increased. Potentially very cheap material was of interest for stealth technology for ground- and water-based objects. A report on the work was submitted to the customer, but due to some reasons, independent of the project team, feedback with potential users was not established.

At present, a more detailed quasi-2D model of the electron-hole ferromagnetism may be proposed [8]. Under the impact mechanical load, the sample with the accumulated high density of dislocations (for example, after three pulses) and relative density close to 1 is subjected to plastic deformation by sliding along the boundaries of nano-sized grains. The input mechanical energy is consumed in particular for charge separation – electron emission from the anion sublattice in the region of grain boundary sliding. A decrease in the volume of the layer of holes with decreased atomic sizes with respect to the ions under the conditions of pressure and shear stimulates the process according to Le Chatelier's principle. Relying on the intensity of the spectra and the input energy, one may easily estimate that not less than 1–10 eV of the input mechanical energy is consumed per one spin, or more than 2–20 eV per one act of charge separation, which does not contradict the physical notions and common sense.

Without ferromagnetic ordering of hole centres in the sliding plane, an inverse reaction of recombination with electrons is inevitable. For example, the own paramagnetic centres of NaF

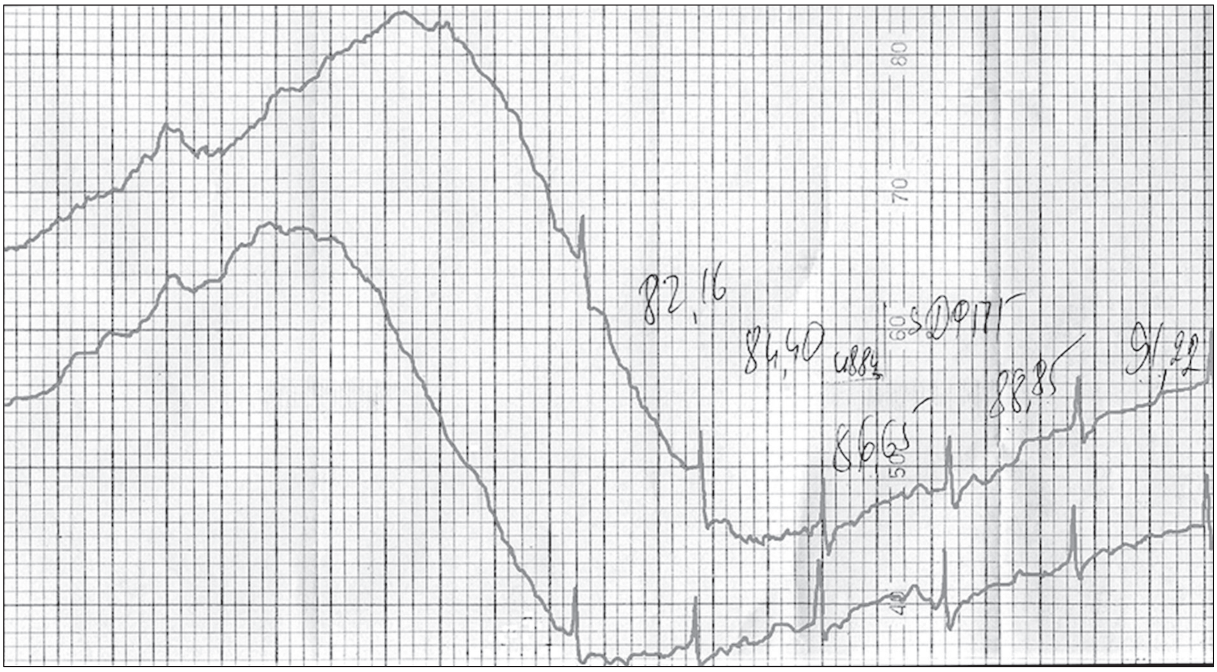

Fig. 1. Absorption spectrum of NaF sample after four acts of loading: top – the parallel orientation of the disc axis in the magnetic field, bottom – the perpendicular orientation. A sextet of narrow lines is the EPR spectrum of Mn^{2+} in MgO reference.

are conserved only at $T < 100$ K. The only possible explanation of the observed ferromagnetic properties of non-magnetic dielectrics is the ferromagnetic ordering of holes (h). Only in this case, the return of electrons to the generation site with the formation of a three-layered structure e-h-e will lead to fixing the ferromagnetic ordering of spins because of the spin forbidden reaction for recombination [24]. The reason for the ferromagnetic ordering of holes with the minimal distance for exchange interaction 2.6 Å for F atoms in NaF and 2.7 Å for O^- in oxides is unknown. For comparison: in iron, where the exchange interaction takes place between the electrons of internal d-shells, interatomic distance is 2.8 Å. Among possible factors affecting the ferromagnetic ordering of holes, we may name the effect of the Earth's magnetic field and the steric factor (because exchange interaction is strongly dependent on the distance).

Figures 1–4 show the original magnetic resonance spectra in the most interesting systems: NaF (the purest initial material and the most intense spectrum after four pulses), KBr (intense spectrum with clearly pronounced anisotropy), NH_4I (is composed only of nonmetals, and the intense absorption spectrum was observed after one pulse), anatase (a combination of ferromagnetic resonance and EPR from paramagnetic centres Ti^{3+}_{is}).

There are many publications dealing with the observations of various kinds of magnetically ordered states in non-magnetic dielectrics. However, all of those studies were carried out using static methods and have a rather low signal to noise ratio. A common disadvantage of these

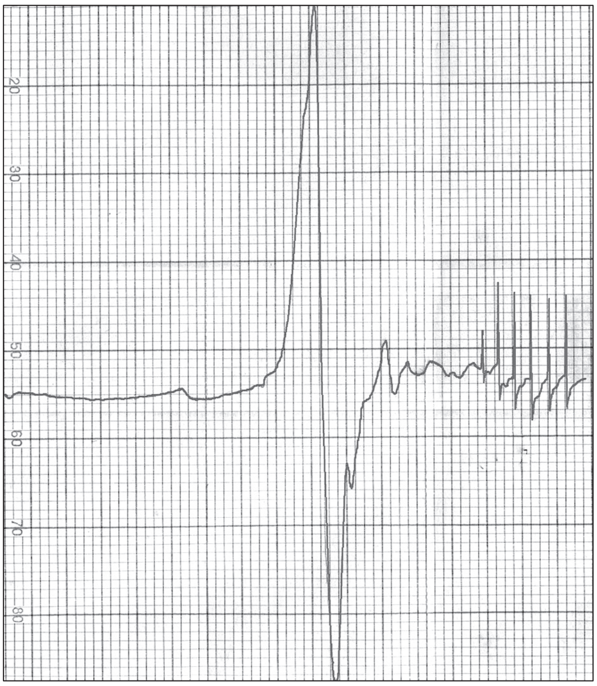

Fig. 2. Absorption spectrum of KBr sample after five acts of loading.

Fig. 3. A region of the absorption spectrum (centre – 3300 G, range – 400 G) of NH_4I sample after three acts of loading: upper line – parallel orientation of the disc-shaped sample in the magnetic field, lower line – perpendicular orientation.

methods in comparison with spectroscopy is the absence of validity: possible effects and different kinds of micro-impurities including those brought into samples occasionally are practically indistinguishable by magnetic susceptibility. One of the most famous and high-quality works is [25], in which ferromagnetic properties were discovered in NaCl and KCl crystals. These properties were attributed to electrons on static dislocations. The magnetization of the crystals obeys the Bloch law with Curie point T_C = 462±1 K for two NaCl crystals and 545 K for KCl crystal. The appearance of free electrons is likely to be connected with mechanical strain in the crystals during cooling. This experimental work was not reproduced by other authors but it stimulated theoretical consideration of dislocation ferromagnetism [26]. It was shown that ferromagnetic ordering in linear chains of spins at T ~ 300 K is possible only in the case of fixed ends and the formation of a flat or spatial network. In our opinion, the ends of linear chains may be fixed with the help of Fe ions; their content in the crystals is several ppm [25]. An extensive review of interesting works (279 references including our work) but with not very large effects is presented in the monograph by Yu. I. Golovin [27]. Results on the effect of magnetic fields on the movement of dislocations and on the mechanical properties of solids are presented, as well as possible mechanisms of the type of a trigger. The activation barrier for overcoming the stopper on dislocations is ~1 eV, while the characteristic value of magnetic interaction is only 10^{-4} eV [27]. A review of modern works on nanopowder ferromagnetism was presented by C. N. R. Rao *et al.* in [28]. By the example of such nonmagnetic substances as CeO_2, Al_2O_3, ZnO, In_2O_3 and SnO_2 with particle size 7–30 nm, it is concluded that ferromagnetism is a universal feature of nanoparticles. Ferromagnetism in the absence of magnetic impurities, disappearing during agglomeration, is attributed to exchange-bound electrons in the traps on the surface of nanoparticles.

The results obtained by us on the electron-hole ferromagnetism were presented for the first time at the International School on Magnetic Resonance in Novosibirsk in 1987 [19]. The work caused substantial interest and a detailed discussion of the results with Academician A. L. Buchachenko finished in an answer to his question: what are the secrets of the accomplished work

a *b*

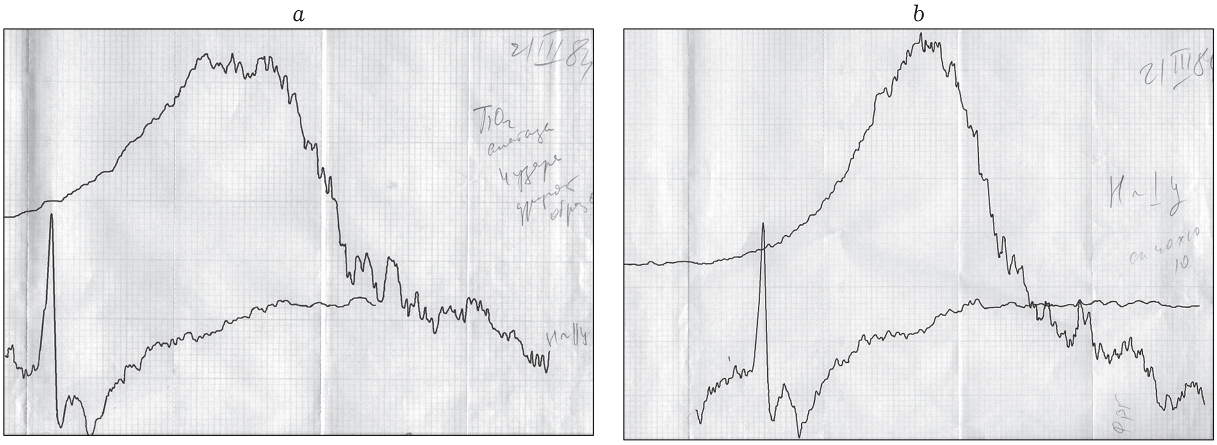

Fig. 4. Absorption spectra of anatase TiO_2 sample after four acts of loading (centre – 3300 G, range – 1400 G): *a* – parallel orientation of the disc axis in the magnetic field, *b* – perpendicular orientation. Lower: the EPR spectrum of Ti_{is}^{3+} from the enlarged fragment of the spectrum in the upper part.

that allowed the observation of intense spectra? The question may be formulated broader: why did thousands of researchers fail to detect so strong effects previously? There are two main reasons. One of them is that the set-up for mechanical loading involved the option of regulating the loading conditions, including the energy and duration (filling the hammer with lead pellets), which allowed us to optimize the conditions and to observe strong effects as a result. Researchers used in similar experiments the devices like mills or anvils, which did not allow obtaining strong effects or proving their origin. In essence, it is the fundamental formulation of the problem – investigation of the response to single-act mechanical loading of the substances - that underlies the success. The second reason is that the measurements of the spectra in powder samples were carried out after mechanical loading on discs that saved the memory of the direction of impact action (or sliding plane). As a matter of fact, due to the high-frequency modulation in order to decrease the noise level, a derivative of the absorption signal is recorded in spectrometers. For this reason, a sharp decrease in the amplitude of the envelope signal and the disappearance of the noise-like spectra are observed after averaging a strongly anisotropic spectrum of ferromagnetic resonance. In this case, a spectrum would appear as a very broad envelope at the background of the usual noise, which is practically impossible to notice and distinguish from the background spectrum of the resonator. As a consequence, it is impossible to optimize loading conditions and to choose the substances with the maximal effect. Our studies started with the purest NaF powder with crystal size ~1 μm, which had finally demonstrated the highest effect, while the first spectra with the intensity hardly distinguishable from the noise were obtained after four acts of loading. The optimization of loading conditions had led to the results under consideration.

The occurrence of intense mechanoemission processes, strongly unappreciated, was confirmed independently by the observation of oxidation-reduction reactions during mechanochemical synthesis [8, 15]. In the theory of the mechanochemical synthesis of oxides, even a separate class of reactions proceeding due to mechanoemission was distinguished. These reactions are characterized by the yields of two orders of magnitude lower with respect to the most rapid processes. The most striking representatives of this class include the reaction

$$Pb_3O_4 + Cu_2O \rightarrow 3PbO + 2CuO$$

in which the initial reagents and products are crystal phases, and no mixed oxides exist.

GAS-DUSTY PLASMA

The dimensions of an elementary 2D-magnetic in the samples demonstrating electron-hole ferromagnetism were estimated as ~1 μm, so the idea was formulated to comminute the samples and to extract ferromagnetic particles in the condensed form. The idea turned out to be not very correct, however, a new air-centrifugal classifier was designed for its implementation. The air flow in this classifier was cycled between the aerosol generation chamber and the collectors of fine fractions; the flow rate could be adjusted to separate submicron particles [29]. The operation principle of all centrifugal classifiers is based on the competition between the Stokes' viscous force and the centrifugal force. However, the work with the classifier showed unexpectedly that the adjustment of the rate of flow carrying fine particles through the centre against the action of the centrifugal force has almost no effect on the powder separation process. Moreover, the productivity of the classifier remained unchanged for the zero flow rate. Examination of the operation of this device had led to the creation of a simple model in which the Coulomb force brings the particles with the maximal charge to mass ratio q/m away against the action of a combination of Stokes forces, centrifugal force, and gravitation (for the case of upward removal). Implementation of the new principle of classifier operation in the installations with different arrangements resulted in the development of a new class of devices called Electro Mass Classifier (EMC) [30]. The Coulomb force appears only in the case if aerosol composed of the charged particles with the same charge sign appears in the generation chamber, so the particles with the maximal charge to mass ratio q/m are expulsed through the centre into relaxation chamber. A dense aerosol composed of charged particles behaves in many respects similar to the dusty plasma in vacuum [31], so it was called the gas-dusty plasma [32]. The presence of charged particles in aerosol had been known long ago [33], but the charges of particles in the dynamic electric equilibrium are very small and are equal to ~2 elementary charge units on the particles 1 μm in size. At the same time, the ionic and electron limit for such a particle is ~$3 \cdot 10^6$ and

~$2 \cdot 10^5$ elementary charge units, respectively [33]. Aerosol science usually treats strongly diluted systems, so Coulomb interactions between the particles have practically no control on aerosol properties The number of works in which some attention was paid to the charged particles in aerosols is very limited [34, 35]. The productivity of the process in an EMC is mainly dependent on the density of the generated aerosol, in which Coulomb interactions become determinative. For instance, the submicron oxide particles like $BaTiO_3$ were removed in the EMC against the action of the centrifugal force of 6000*g*. Rough estimations show that under the conditions characteristic of laboratory EMC micro-separators the sufficient number of excess charges per a particle 1 μm in size is $n \times 10$. Many mechanisms of particle charging are known [33], leading to different signs depending on conditions and materials, including the materials of generation chamber wall and the rotor blades. However, during 35 years of EMC operation with many thousand different powders, during separation we did not observe any case of the change of the charge of particles flying to the fine fraction (a consequence of such an event would be a decrease in the productivity to zero and then again an increase). This means that a prevailing mechanism of particle charging exists, while all other ones make definite contribution affecting the productivity either to one side or to another. It may be assumed on the basis of the results obtained on ferromagnetism in non-magnetic dielectrics that the major contribution into particle charging is made by mechanoemission of electrons. In this case, fine particles carry the positive charge away to the relaxation chamber, while the negative charge should get accumulated in the generation chamber. If the chambers in the EMC are insulated from each other electrically, then the transport of aerosol should be accompanied by the appearance of the potential difference. Multiple attempts to measure the electric current between the chambers during material separation failed. However, in 2014, a substantial potential difference was detected during the separation of semiconductor SiC powder with the size of crystal particles equal to several micrometers. The fact is that particle discharge and the charge exchange between the chambers proceed through several channels including the gas environment. During the separation of dielectric powders, the excess charge remaining on the deposited particles relaxes too slowly and mainly through the gas environment. During the separation of metal powders, the excess charge is not large, and the gas medium removes it rather efficiently. In the powders of solid semiconductors like SiC with the optimal particle size, efficient charging and rapid discharging occur on the metal surface of the relaxation chamber, which ensures the appearance of the potential difference and provides an unambiguous confirmation of the principle of EMC operation.

Modeling of generation and relaxation of the gas-dusty plasma is a too complicated task even for supercomputers. The number of parameters is unacceptably large even in the most simplified model. In real powders with non-spherical particles, the appearance of strong electric interactions between the particles in a dense aerosol is possible even in the absence of excess charge because the electron output energy depends on surface curvature. At the same time, the experience accumulated in this area and a series of model experiments allow us to predict the results to a substantial extent. In scaling from rotor diameter of 0.2 m in a laboratory EMC to the pilot installations with rotor diameter ~0.6 m, the deviations of separation parameters from the expected values turned out to be acceptable.

The most demonstrative results of model experiments in the EMC will be listed below.

1. A stochastic process of relatively dense gas-dusty plasma goes on in an EMC. Charged particles in usual centrifugal classifiers bring a decisive contribution into the separation process with particles 10 μm in size and smaller, but particle charge is not yet taken into account in the standard description of the process and in the calculations of the equipment.

2. The generation of gas-dusty plasma has a pronounced threshold nature. The threshold flow rate depends on the material, particle size, rotor design (the degree of turbulence) and the arrangement of generation chamber, but the characteristic value is ~10 m/s.

3. Generation of the gas-dusty plasma and its separation are observed in all types of materials: in dielectrics, semiconductors, metals including silver.

4. An increase in the volume of the relaxation chamber enhances the productivity of separation, while other parameters are conserved. The gas-dusty plasma is characterized by peculiar *pressure* which decreases with an increase in the distance from the generation zone and with time because of the transfer of excess charges into the as envi-

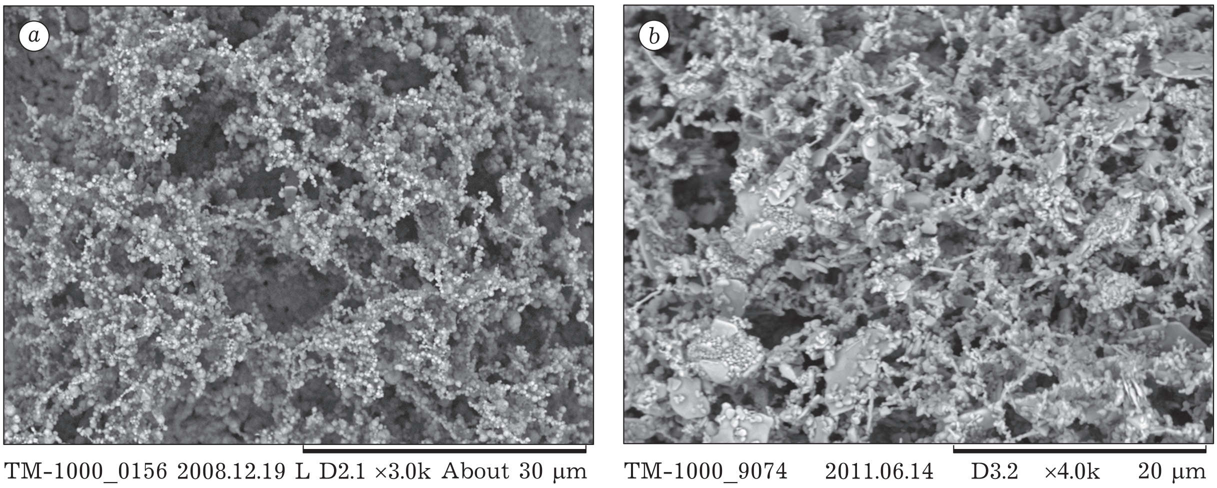

Fig. 5. Nickel (*a*) and silver (*b*) powders with low-density framework structure, accumulated in the collector of fine fractions in EMC.

ronment through emission or interaction with air ions.

5. The effect of the gas environment turned out to be very remarkable. Separation does not proceed at high humidity because the generation of the gas-dusty plasma becomes impossible. At very low humidity, the generation of the aerosol is maximally efficient, but charge relaxation proceeds slowly – mainly through metal surfaces because of the low concentration of air ions. There is an optimal level of humidity for productivity and quality of separation; it depends on the nature of the material and its dispersity. The effect of the vapour of polar organic solvents is very complicated.

6. The deposition of charged particles in the relaxation chamber on the electrodes with the electric field strength of 6 kV/cm did not demonstrate noticeable differences, but magnetic particles under the same conditions were deposited into a permanent magnet. In other words, the effect of excess charges of particles on the deposition is substantially lower than the effect of their dipole moments. This conclusion is confirmed independently by the appearance of dendritic filaments ~1 cm long composed of micrometer-sized particles in the relaxation chamber and by the formation of highly porous framework structures with relative density ≥ 1–2 % as a result of deposition (Fig. 5) [32, 36]. The generation of a large dipole moment on the particles may be explained for crystal particles: some electrons are emitted from the impact region and some are carried away inside the solid according to the dislocation mechanism. However, a large dipole moment is also observed in dislocation-free particles. The dipole moment is likely to be formed both at the moment of mechanical loading and in the process of particle coagulation in aerosol before deposition (Fig. 6).

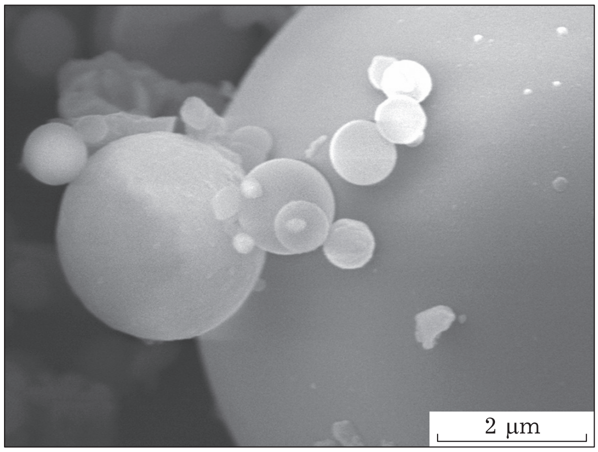

Fig. 6. Demonstration of the coagulation of fine particles on the sample of glass microspheres from fly ash.

7. Separation of a powdered mixture of insulin with crystal size ~100 μm and Fe_2O_3 with particle size ~1 μm resulted in the accumulation of the fine fractions of both components in the collecting unit. This fact may be understood if the prevailing mechanism of particle charging is the mechanoemission of electrons.

APPLICATIONS OF EMC

Various arrangements of the installations are possible: *plasma outflow upward*, *plasma outflow downward*, and even to all sides, which allows us to term the EMC as a unique polyfunctional technique for processing dry powder materials. The most important features and characteristics determining possible applications are:

1. Combination of different options depending on arrangement – separation by particle size, separation by the properties of materials, grinding, mechanical activation of the surface, spheroidization of the particles of plastic materials, homogenization, disaggregation, formation of especially dense coatings (in the generation chamber) and highly porous ones (in the relaxation chamber).

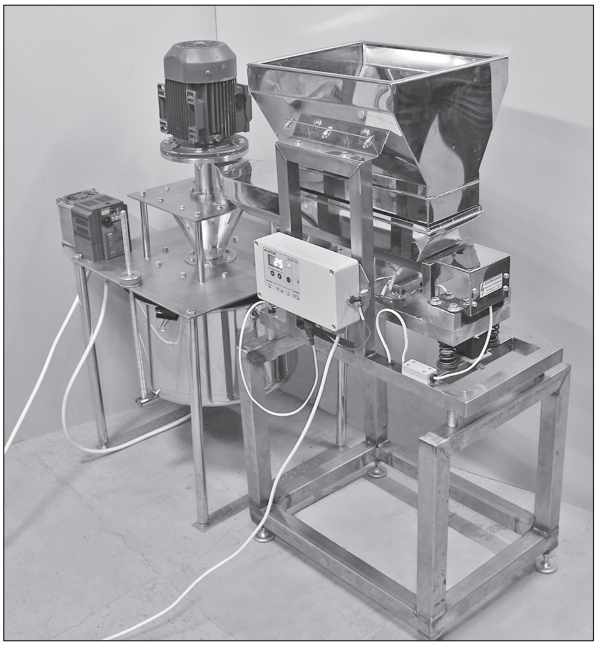

Fig. 7. EMC installations for processing of shungite – a natural source of nanocarbon materials.

2. Operation in the closed volume with controlled atmosphere, pressure and temperature, in other words, EMC provides a fully ecologically safe technique that allows one to work even with dangerous substances.

3. The operational capability of EMC for the overwhelming majority of materials is within the particle size range from 100 nm to 100 mm (Fig. 7). EMC is inefficient in the case of friable and fine dispersed agglomerated powders because of the impossibility of aerosol generation due to strong inverse aggregation. For some systems, the introduction of the coarse activator particles allows ensuring aerosol generation.

4. Various operation modes: continuous, discrete, and discrete-continuous.

5. Unlimited number of the fractions of products.

6. Due to controllable turbulence and the closed volume, EMC is the best technique for dust removal from materials (Fig. 8), after which the selective separation (Fig. 9) and the development of additive technologies become possible [37–40].

7. Enormous productivity range – from 1 g of the sample in the discrete mode, which is extremely important for research purposes, up to 5–10 t/h in the continuous production. Even the treatment of the dust-like and technogenic raw materials is technically and economically possible with a battery combining several EMC devices with common systems of raw material supply and product collection.

8. Relatively low energy consumption due to the combination of functions at the rotor.

9. The possibility to make large EMC as building structures with the low cost of the equipment.

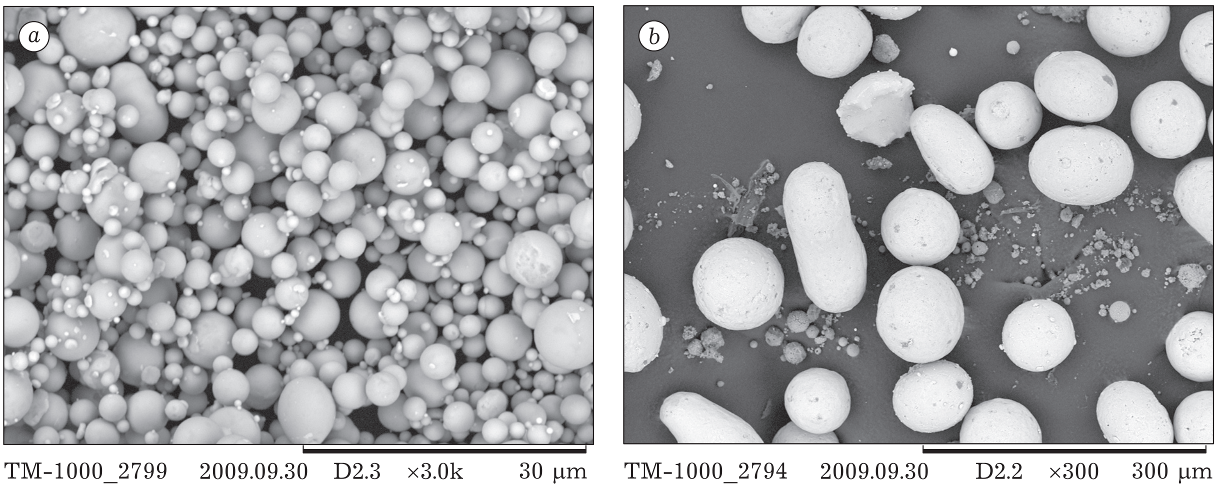

Fig. 8. Example of efficient dust removal from tin powders in EMC: *a* – dust, *b* – coarse fraction.

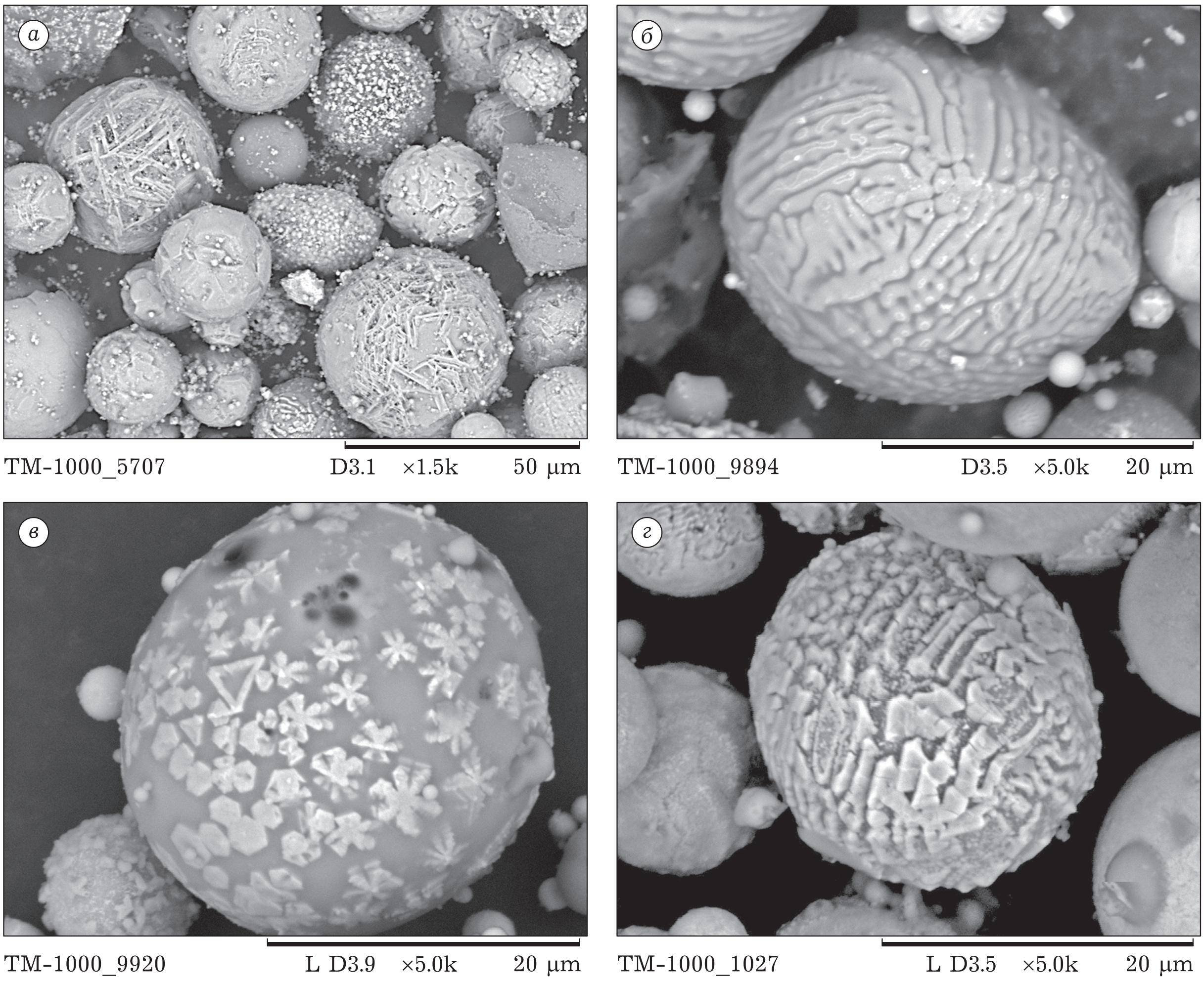

Fig. 9. Demonstration of the selective separation of magnetic spheres with total content about 2 % at the triboelectric separator with magnetic option after the removal of dust from fly ash in EMC: *a* – from the brown coal ash (Krasnoyarsk); from coal ash: *b* – Novosibirsk, *c* – China, *d* – the USA.

10. Compatibility with other devices in technological lines.

According to the accumulated experience and market analyses, only EMC technique is able to solve the problem of profitable utilization of industrial fines through their integrated processing [38, 39], as well as dry concentrating of natural raw materials [40, 41]. On the other hand, laboratory EMC microseparators in combination with planetary mills allow one to develop new composite nanomaterials and implement the nano-architectural approach in materials science [42–43].

CONCLUSION

The processes of mechanoemission in solids are obviously underestimated by the scientific community. A substantial part of the input mechanical energy in solids is consumed for charge separation followed by transformations. The observation of the intense spectra of electron-hole ferromagnetic resonance improves the reliability of many weak magnetic effects discovered by present, and makes us pay more attention to the possible mechanoemission of neutrons. The formation of the dynamic state connected with mechanoemission – *gas-dusty plasma* – in EMC may be used to solve many complicated applied tasks within a broad range from the design of nanomaterials with different architecture to the integrated dry processing of dust-like raw materials and wastes.

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