Phenomenology, Kinetics and Application of Abrasive-Reactive Wear during Comminution (Overview)[†]

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Abstract

Valuable information on the phenomenology of mechanical activation will be obtained from the accurate characterization of wearing processes that take place within mechanochemical reactors. Favoring the contamination of reactant powders with material from a reactor's debris, for a long time such processes represented one of the greatest limitations to practical mechanochemistry applications. We will focus on two related aspects of mechanochemical processing by grinding in a ball mill: (i) nanoscale wear of the treated substances and of the milling tools (balls and container wall); and (ii) deposition of a powder coating on the surface of the milling tools (self-lining phenomenon). A new technology called abrasive-reactive wear (ARW) has been developed that utilizes wear debris as an integral component of the reaction system rather than treating it as a harmful impurity. This technology is applied to the preparation of nanocomposites and to the processing of mineral raw materials and industrial byproducts. This review includes preparation experiments, material characterization, ARW kinetics and simulation. Besides developing new technologies, ARW will contribute to a better understanding of the mechanochemical or mechanical alloying process in general.

Keywords: Mechanochemistry, material of milling tools, abrasive-reactive wear, nanocomposites

1. Introduction

The mechanical activation (MA) of powders, usually carried out in suitably designed ball mills that are considered mechanochemical reactors (MR) essentially consists of the repeated mechanical loading of powders trapped between the colliding surfaces of the milling tools¹⁻⁴⁾. The local compressive and shear events create hot spots and induce plastic deformation and fracturing of the particles⁵⁻⁷⁾. Under such circumstances, powder particles undergo continuous comminution associated with interface renewal processes. These promote the occurrence of physicochemical transformations including microstructural refinement down to nanometer size⁸⁻¹²⁾.

Contamination due to the abrasion of milling tools is an inevitable problem of conventional MA in MR; the level of contamination can reach several percent and can rarely be kept below a few tenth of a percent⁴⁾. Many authors mentioned this problem in their works on mechanochemistry. Moreover, some concrete examples of the possible participation of the milling tools' material in mechanochemical processes were reported¹³⁻²¹⁾, but these works have not been followed up on.

In¹³⁾, the Mössbauer effect was used for studying MA processes of quartz. The metal iron, which contained 2.17% of isotope ⁵⁷Fe, was introduced into quartz during the process of MA as a result of the steel milling tools of a disintegrator (pin disc mill or UDA) being worn by the particles of quartz at their relative linear speed of impact up to 270 m/s. Experiments on the mechanical activation of quartz were carried out in a vacuum and in air. It is shown that the Mössbauer effect can be used successfully for studying the mechanochemical reactions of quartz with an

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iron material of disintegrator milling tools. In¹⁴, the quantitative characteristics of the steel material wear of milling tools dependent on MA time were determined for the first time with the purpose of mechanochemical opening of sulfide and arsenide minerals.

In¹⁵, the participation of the milling tools' steel material in the process of mechanochemical sulfidizing of some oxidized copper minerals in the presence of water was shown and the sulfidizing mechanism was established for the first time. In¹⁶, the influence of mill power and grinding environment on the contamination of quartz by iron during vibration grinding was studied. It was found that the Fe content in ground powders increased with increasing specific milling energy. The specific contamination expressed as the ratio of Fe content to newly created surface area depended upon the physical properties of the grinding environment. The influence of grinding conditions on the state of the iron in the products of grinder wear was investigated by Mössbauer spectroscopy and by measuring the magnetic susceptibility of the ground powders. It was shown that the iron produced from grinder wear is present in two main forms: as a magnetically ordered form identical with the basic material of the grinder and in a form of finely dispersed iron compound showing superparamagnetic behavior. Based on the results obtained, the formation of a silica-supported iron or iron oxide catalyst was presumed.

In¹⁷, the wear of high-carbon low-alloy cast steel balls during the grinding of a chalcopyrite ore was evaluated under different experimental conditions. The role of oxygen in enhancing ball wear during wet grinding is emphasized. Contributions from corrosion and abrasion towards ball wear are quantified in terms of ball wear rates as a function of time, particle size and gaseous atmosphere in the mill. In¹⁸, quartz powders prepared by MA in a planetary mill in the presence of monohydric or dihydric alcohols were found to exhibit magnetic properties as the result of abrasive wear of the material of the steel milling tools. The magnetic susceptibility of milled quartz depends on the milling time and the amount of additions. The material was shown to undergo aging: its susceptibility and electron paramagnetic resonance spectrum vary during storage. The magnetization of quartz is interpreted in terms of Fe-containing clusters present in the amorphized surface layer. In¹⁹, the interaction of the sample with wear products from milling tools made of steel, tungsten carbide and strengthened ball bearing steel (ShKh15) is investigated by means of Mössbauer spectroscopy, X-ray diffraction and gravi-

metric measurements. It is stated that under identical conditions, ShKh15 steel is the most resistant to wear and the least prone to participate in mechanical alloying. It is shown that when choosing materials for milling bodies for the investigations of mechanical alloying, one should take into account a condition that ensures the delivery of reliable information: an increase of the mass of the sample under investigation should not exceed 10% during mechanical treatment.

Research of new nanocomposites prepared by the non-conventional mechanochemical route under the abrasive-reactive wear conditions was stimulated by the works of^{20,21}.

In the work of Goya et al.²⁰, who followed the phase evolution of CuFe_2O_4 during high-energy ball milling in a steel vial, it was shown that a two-phase mixture consisting of magnetite and a spinel solid solution ($\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$) yields the final product of the mechanical treatment of Cu-ferrite. This indicates that the high-energy milling of the oxide generates a complex series of solid-state transformations, including mechanochemical decomposition and reduction. In view of the fact that the milling is done in air, the appearance of reduced phases in an oxide matrix is a surprising experimental result. Although several mechanisms have been proposed for the reduction processes occurring during high-energy milling, to the best of our knowledge, no conclusive explanation for mechanically induced redox reactions has been given yet. Identification of the factors representing the main driving force for mechanically induced redox processes in complex oxides, the elucidation of the microscopic mechanism(s), and the determination of rate-determining steps of reduction therefore represent a major challenge for research in mechanochemistry and require further efforts.

In²¹, the product of ball milling magnetite and amorphous silica (40-mole % Fe_3O_4 in SiO_2) for an extended period of time (800 h) in a closed vial was investigated by Mössbauer spectroscopy, X-ray diffraction and infrared spectroscopy. It was found that the milling induces an extensive reduction of Fe(III). The material constitutes a mixture of ultrafine Fe-rich spinel particles (magnetite/maghemite) and amorphous Fe(II)-containing silicate with a magnetic transition temperature of approximately 25K. The amorphous phase has a rather high Fe content and is distinctly different from the initial amorphous silica.

On the other hand, for example, the chemical activity of ammonium thiocyanate or the high hardness of boron resulted in wear to the steel material of the milling tools of the MR, the particles of abraded iron

entered into mechanochemical reactions with the treated mix of reagents²²⁻²⁵, and the quartz and other mineral particles were modified by abrasion from iron compounds¹³⁻²¹.

From these scattered reports it is evident that regular research of the participation of a material of milling tools in the course of mechanochemical reactions was not carried out. A novel strategy for their exploitation as an effective synthetic route will be described which will permit the preparation of fine materials for high-tech purposes²⁶. The choice of focusing on abrasive-reactive materials is motivated by the possibility of synthesizing them via both gradual⁴ and combustive⁵ mechanochemical reactions starting from elemental powders. The prospect of their realization does not cause doubts. In a method offered by us of obtaining nanocomposite powders on a copper, graphite and diamond basis, only copper fittings will be used. As against the traditional realization of mechanochemical reactions in mixes of powders with the sizes of initial particles ~50 microns^{4,5,27,28}, the synthesis, for example, of nanocrystalline final products proceeds for hundreds of hours of MA²⁷, and owing to participation of the nanosized material resulting from the abrasive wear of milling tools, a significant reduction of this time could be expected. Recently begun intensive research of mechanochemical reactions with the participation of a material of milling tools not only confirmed this assumption, but also revealed many other advantages and prospects of their realization²⁹.

Sometimes it is possible to select the material of the milling tools in such a way that the wear debris becomes a beneficial component of the intended product. We plan to carry this possibility to the extreme: We will develop a new technique called abrasive-reactive wear (ARW) that uses the material of the milling tools as a reactant that becomes a major component of the product, not just a tolerable impurity. This innovative new approach has not been considered by any other laboratory. It opens the door to applications of the ARW phenomenon to obtain nanocomposite powders and for carrying out the synthesis of chemical compounds, functional materials, and for processing mineral and man-made raw materials. It will be shown here how the wearing of milling tools could instead provide an alternative synthetic route to materials of technological interest^{26,29} such as the Cu-diamond composites that possess a high thermal conductivity³⁰.

We must note that throughout the world, there is currently no direction of research analogue to that

pursued by us. From the viewpoint of its application for the preparation of new functional materials, the work will be innovative and useful. The probable scopes of the ARW method stated in the paper lead us to believe that it can find specific application in various areas of modern technical mineralogy and tribology.

2. Experimental

2.1 Planetary mills with steel fittings and MA

The relative velocity W of collisions between milling tools is given by the equation^{2,6,31-36}

$$W = 2\pi\omega_1 l_2 [(k+1)^2 + m^2 - 2m(k-1)\cos\varphi + (m+1)^2]^{0.5}; W_n = W\sin\varphi; W_t = W\cos\varphi \quad (1)$$

where $\cos\varphi = -(1+k)/m$ determines the angle of ball rebound from walls. The geometric factor $m = l_1/l_2$, where l_1 and l_2 are the radii of the carrier and drum, respectively; the kinematic factor $k = \omega_2/\omega_1$, where ω_2 and ω_1 are the number of revolutions of the drum and the opposite number of carrier revolutions, respectively. An analysis of the interaction of milling tools must be performed taking into account both the normal component W_n and the tangential component W_t of the W ³³. W_n determines the conditions of the interaction of particles in the layer. W_t determines the conditions of abrasive wear and mechanochemical processes on the frictional contact between milling tools and treated particles.

For the mechanical treatment (the process time τ was varied over the range 5-240 min), we used:

- A three-drum planetary mill from "NPO Mekhnobr", the characteristics of the mill were^{33,34}:
 $m = 2.3$ ($l_1 = 11.5$ cm and $l_2 = 5.0$ cm); $k = -1.7$ ($\omega_2 = 20$ s⁻¹ and $\omega_1 = 11.7$ s⁻¹); $W \approx 1700$ cm/s, $W_n \approx 500$ cm/s, $W_t \approx 1600$ cm/s; the drum volume $V = 450$ cm³; and the working part of the surface of the drum $\Pi_d = \pi l_2(2h+l_2) \approx 250$ cm², where $h = 5.5$ cm is the drum height. The ball radius was $R = 0.5$ cm, their density $\rho = 7.8$ g/cm³, number N , and the totaled surface area $\Pi_b = 4\pi R^2 N$.
- An AGO - 2 water-cooled two-drum planetary mill with the characteristics^{25,35,36}: $m = 1.7$ ($l_1 = 5.3$ cm and $l_2 = 3.1$ cm); $k = -2.4$ ($\omega_2 = 29$ s⁻¹ and $\omega_1 = 12$ s⁻¹); $W \approx 1100$ cm/s, $W_n \approx 900$ cm/s, $W_t \approx 630$ cm/s; $V = 140$ cm³, $\Pi_d \approx 150$ cm² ($h = 4.6$ cm); $R = 0.2$ cm. To provide more efficient processing, we used all four possible orientations of the mill axis: vertical, horizontal and $\pm 15^\circ$ to the latter in each case.
- An EI - 2 $\times$ 150 two-drum planetary mill characterized by^{2,26} $m = 1.8$ ($l_2 = 2.9$ cm), $k = -1$ ($\omega_2 = \omega_1 = 14$ s⁻¹), $\cos\varphi = 0$ and $W = W_n \approx 850$ cm/s, V

$=150\text{ cm}^3$, $\Pi_d \approx 130\text{ cm}^2$ ($h = 5.6\text{ cm}$); $R = 0.2\text{ cm}$.

The powdered mixtures had previously been ground and homogenized for 15-30 min in a Fritsch Pulverisette mill fitted with steel (a mortar of diameter 9.5 cm + 1 ball of diameter 5.2 cm) or agate (9.2 cm and 7.1 cm, respectively)^{37,38} elements. We selected preparation of nanocomposites under various conditions of MA of the *A* (material of milling tools) – *B* (abrasive) and *A* – *B* – *C* (reagent) systems (e.g. iron-quartz; iron-diamond, iron-quartz-sulfur, iron-quartz-graphite, copper-diamond-graphite, etc.) in a MR as an example of ARW, cf.³⁹. The ratio between the weight of the treated substances ($M = M_A + M_B + M_C$) and the mass of the ball load (M_b) was varied. Let ρ_A , ρ_B , and ρ_C be the densities. The uniform self-lining of milling tools (balls and inside drum walls) by a batch mixture layer occurs during MA^{2,40,41}. The calculated lining thickness is^{12,34,39}

$$\delta = (\rho_B \rho_C M_A + \rho_A \rho_C M_B + \rho_A \rho_B M_C) / \rho_A \rho_B \rho_C (\Pi_d + \Pi_b) (1 - p) \quad (2)$$

$$\delta_C = M_C / \rho_C (\Pi_d + \Pi_b + \Pi_{A+B}) \quad (3)$$

Here, the porosity of the lining p is taken to equal that of a close packing of differently sized spherical particles ($p \approx 1 - \pi/4$). In a number of cases, *C* – substance (e.g. graphite or sulfur), as the most plastic and pliable components, covers all metallic (*A*) and abrasive (*B*) surfaces with a continuous layer with a thickness calculated by Eq. (3), where the areas *A* and *B* particles are Π_{A+B} ^{39,42}.

2.2 Product and process characterization

The initial mean particle size (R_0) was determined by optical microscopy (NU-2E) on parts of the starting homogenized specimens for MA, and was in the range 0.01-0.025 cm. MA products were studied by the standard XRD, DTA, Mössbauer (MC1104EM), Raman (Dilor/OMARS), infrared (Satellite FTIR) and electron microscopy (JSM-6380 and LEO-1550) methods. MA amorphous samples were also isothermally annealed (2 h) in a flow of argon ($\sim 1\text{ cm}^3/\text{s}$) in alundum crucibles with graphite plugs and titanium sponge placed upstream of the crucibles in the heated area of the quartz tube to remove the possible oxygen impurity from argon using a new heating stage for high-temperature (up to 1600°C) investigations⁴³. The degree of grinding was determined by the thermal desorption of argon with additional disaggregation^{15,34}. Possible iron forms in some specimens (e.g. in quartz particles) were determined by acid etching of the material according to³³. Washed samples were studied by routine analysis methods. ARW kinetics was studied by two methods: weight, with accurate

measurement of drum weight and ball loading before and after experiments not less than 0.01 g; and volumetric in the case of diamond-containing MA products, on reaction of samples with an acid.

3. Results and Discussions

3.1 ARW processes caused by the MA of quartz

One of the purposes of this work was to study the influence of the material of milling tools on the MA of quartz in MRs with steel fittings. We selected these objects of study because MA quartz and mixtures based on it exhibit ferromagnetic properties and are distinguished by good sorption ability toward organic substances, the synthesized sorbents were used to collect petroleum spill over water, high water purification, etc.^{44,45}. A ball mill from “NPO Mekhanobr” was used, the ratio between the weight of ball loading M_b to that of quartz M was set equal to 4 at $M_b + M = 480 + 120 = 600\text{ g}$. The number of balls $N = 120$, and the totaled surface area $\Pi_b \approx 370\text{ cm}^2$. According to Eq. (1), abrasion conditions should be given preference over impact conditions for this mill. In several control tests (Fig. 1), we also used an AGO-2 mill and fused quartz (from the standpoint of interpretation of XRD data, amorphous materials are the most suitable abrasive components). It follows from³³ that $\sim 90\%$ of iron is present in quartz in an acid-soluble (metallic and magnetic) form.

The total wear of steel mill fittings can amount to $\sim 5\%$ ($\sim 7\text{ g}$), and the dependence of the amount of worn iron on the time of processing is not linear (Fig. 2). The deviation from linearity is caused by the self-lining of milling tools to a degree that increases as the specific surface area of the material under

Fig. 1 X-ray pattern of fused quartz (3 g) processed for 12 min in an AGO-2 mill (number of balls $N = 400$). The size of worn particles for a material of milling tool $\sim 10\text{ nm}$ ^{33,34}.

Fig. 2 ARW kinetics under MA of quartz in “Mekhanobr” mill by expression $K \times \tau^n = 1.8 \times \tau^{0.23}$ is described in⁴⁹.

processing grows^{33,46}. This partially protects milling tools from wear.

Temperature and pressure pulses^{2,3,7} favor the occurrence of chemical reactions involving the material of milling tools, substance being processed, and medium^{33,34}. As the reaction between Fe and SiO₂ is forbidden, we consider the possibility of steel oxidation by air; the drums of our mill did not have vacuum gaskets, and processing occurred under air access conditions, as distinguished from control tests with the AGO-2. As a result of abrasive and oxidative wear, Fe and FeO are formed as nanoscale particles and should be adsorbed on much larger quartz particles.

On the other hand, part of the surface layer of quartz particles subjected to MA becomes amorphous (Fig. 3). The mechanism of the transition to the amorphous state and the thickness of the amorphous layer have long been the subject of discussions^{1,33,34}. The question of the form in which iron is contained in activated quartz particles is the most interesting one. For this reason, along with modeling, we used the most informative methods for quartz studying, namely Mössbauer and infrared spectroscopy.

MA samples washed to remove the elemental iron only contain quartz particles with a very insignificant iron content in an acid-insoluble form (up to ~0.6% or ~0.75 g based on iron). It follows that acid-insoluble³³ iron silicates formed during processing approximately in an amount of 2 g can only occur on the surface of quartz particles. The estimated mean thickness of this layer is ~1 nm³⁴.

The Mössbauer spectra, Fig. 4 (see also infrared, Fig. 5), of iron atoms in iron oxides are characteristic sextets resulting from the magnetic splitting of nucleus levels.

Our samples give additional lines, which are evidence of changes in the character of bonds between iron atoms and their environment. A quadrupole doublet, whose hyperfine coupling parameters show that iron occupies two nonequivalent sites in the quartz lattice, describes the internal part of the spectrum. For the first doublet, the isomeric shift and quadrupole splitting parameters show that iron Fe³⁺ ions have an octahedral oxygen environment characteristic of iron oxides in the super paramagnetic state.

Fig. 3 Electron micrograph of the quartz particles after MA: general view (left); separate particle (right).

Fig. 4 Mössbauer spectra of MA quartz particles processed 30 (left) and 90 (right) minutes.

Fig. 5 Infrared spectroscopy of the MA quartz.

The hyperfine coupling parameters of the second doublet can be attributed to Fe^{2+} ions in the high-spin state. The population of these two sites by iron ions depends on the duration of MA, and the presence of such iron forms in quartz can only be explained by the formation of iron silicates. The infrared spectra of the initial quartz samples and MA samples for 15 min indirectly substantiate the formation of iron silicates. There were no differences between the Si – O – Si and O – Si – O bands in the spectra of different samples. However, a band at $\sim 833\text{cm}^{-1}$ appeared in the MA sample; this band was assigned to the Si – O – Fe bond in³³⁾.

At high temperatures³⁴⁾, the formation of iron metasilicate ($\text{FeO} + \text{SiO}_2 = \text{FeSiO}_3$) in the FeO – SiO_2 system is more favorable thermodynamically and

kinetically than the formation of iron orthosilicate ($2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4$), because the reaction occurs in the presence of excess quartz. As a separate phase of iron silicates is not observed, they can only occur in the amorphous layer on activated quartz particles. The empirical mean thickness of the layer of iron silicates on the surface of quartz particles if iron silicates are distributed uniformly is $\sim 2\text{ nm}$ ³³⁾.

3.2 ARW in abrasive – graphite/sulfur systems

Extending the ARW method is of particular interest as regards the use of carbon^{26,35)}, in particular graphite³⁷⁾, and sulfur³⁸⁾, which have unique physicochemical and mechanical properties^{29,36,47)}. Carbon and sulfur in ARW can open up a new line in making nanocomposite materials on a carbide^{4,19,24,25,31)} or

sulfide^{1,5,8,9,14,15,27,28,39} basis. This method can also be successfully used in the utilization of dust formed in decarbonization and desulfurization of the coke-oven gas formed in the coke and by-product industries³⁷. The accumulation of sulfur at oil refineries and plants processing natural gas also makes its utilization a matter of current interest.

Cementite (Fe_3C) is commonly obtained by the MA of mixtures of iron and carbon powders, with subsequent thermal or arc-plasma processing of the MA products^{48,49}. Sulfides are, as a rule, obtained from elements on MA and heating^{5,8,9,27,28}. However, the morphology and the homogeneity of the target products are not always of the required level. It depends on a number of factors and, in particular, on the area and state of the surface of the starting reagents. The use of MR eliminates these drawbacks. At present, iron sulfides, especially those of nanosize^{8,9,27,28}, are applied in power cells with a high energy density, in photoelectrolysis and solar power engineering, and in the synthesis of superconducting, diagnostic and luminescent materials and chalcogenide glasses.

The results of the simulation of mechanochemical reactions involving sulfur⁴² show that the most important process for the synthesis of sulfides, e.g., ZnS^{50} , is the plastic flow of sulfur. The heat pulse in the shock displacement of molten sulfur is determined by the thickness of layers on the surface of

Zn particles lined with softer sulfur. The thinner this layer, the higher the temperature and the faster the amorphization of sulfur (polymerization with a transition to the glassy state). However, the occurrence of this process has not been confirmed experimentally. Therefore, to substantiate the theory⁴², it was necessary to choose a system for MA that would contain an inert amorphous component alongside crystalline sulfur. Ordinary glass and fused silica are suitable for this purpose. Confirmation of the mechanochemical polymerization of sulfur is also the goal of this study. The MA was performed in an AGO-2 mill ($N = 400$, $\Pi_b \approx 200\text{cm}^2$). Graphite or sulfur were introduced in amounts of 0.3-1.6 g into a crushed amorphous (slide glass or fused silica) or crystalline (quartz) abrasive taken in an amount of 3.0 g. The annealing temperatures chosen were considerably lower than the temperature of cementite formation³⁶, i.e. were equal to $660 \pm 5^\circ\text{C}$ and $960 \pm 10^\circ\text{C}$.

The XRD patterns of the system constituted by fused quartz and graphite after MA is shown in **Fig. 6a**. It indicates an amorphization of graphite and wear of steel milling tools, see **Fig. 1**.

In the course of MA of the system with $\alpha\text{-SiO}_2$, quartz reflections are preserved, but with significant broadening and decrease in intensity compared with the initial homogenized sample. Wear of steel grinding tools also occurs (see a fragment of the spectrum

Fig. 6 XRD patterns of the system constituted by quartz (3g) and graphite (1.5g).
 (a) Fused quartz, MA duration (τ) 90 min;
 (b) α - Quartz, MA duration 90 min;
 (c) Annealing of MA sample (a) for 2 h in argon at 960°C .

in **Fig. 6b** at $2\Theta = 44.68^\circ$.

In both low- (660°C) and high-temperature (960°C , **Fig. 6c**) annealing, cementite crystallizes (PDF 75-910) from the amorphous phase. However, the degree of cementite crystallization from the amorphous phase for samples annealed at 660°C is lower than that for the samples annealed at 960°C . The presence of residual nanoscale iron particles in the samples (**Fig. 1**) is confirmed by the following: the peak of cementite at $2\Theta = 44.72^\circ$ overlaps the base reflection of $\alpha\text{-Fe}$, but not its reflection at $2\Theta = 82.4^\circ\text{--}82.5^\circ$. In annealing, a partial crystallization of graphite also occurs (halo at $2\Theta = 26^\circ$ in **Fig. 6**). Similar results were obtained for the system with quartz. It can be stated that the nanocomposite $\text{Fe-Fe}_3\text{C-C-SiO}_2$ is formed in the course of the MA of quartz-graphite systems.

Experiments on the MA of sulfur crystals (weighed portion 2 g) only were carried out under identical conditions. The XRD data for samples of MA sulfur (MA duration of up to 180 min) show that no structural transformations in sulfur take place [38]. All the reflections are preserved without any appreciable change in their shape and relative intensity (PDF 83-2285), except for the absence of a halo associated with the presence of amorphous particles of fused quartz or glass. The situation changes (**Fig. 7a**) when sulfur is treated in the presence of inert glass particles.

Fig. 7 XRD patterns of systems with sulfur.
(a) Glass (3g) and sulfur (0.4 g), $\tau = 135\text{min}$;
(b) Fused quartz (3g) and sulfur (1.6g), $\tau = 135\text{min}$.

Fundamental changes occur in the MA of samples based on fused quartz: Pyrite is formed (FeS_2 , PDF 71-2219; **Fig. 7b**). The hardness of quartz particles is considerably higher than that of steel, and its softening point substantially exceeds that of glass. In this case, amorphization of sulfur (absence of reflections of excess sulfur in **Fig. 7b**) and its chemical reaction with iron nanoparticles (which have already appeared in a significant amount as a result of the ARW of steel accessories) to form pyrite FeS_2 occur simultaneously. The formation of just FeS_2 is due to the excess of sulfur in the MA samples.

Using the method^{14,27} and the XRD data, we also calculated the sizes of crystal blocks and the extents of distortion in the structure of the resulting pyrite (and Fe particles). The parameters of fine crystal structure were calculated from the half widths of the diffraction peaks (220) and (440), which are commonly associated with FeS_2 ⁴⁷. To determine the instrumental broadening, we used the profile of lines of crystalline FeS_2 . The resulting size of blocks in FeS_2 was about 24 nm (~ 10 nm for iron particles), and the extent of distortion 1%. Similar results were obtained in²⁷, but after more than 110 h of MA of a 1:2 mixture of powders of Fe (starting particle size $\sim 0.05\mu\text{m}$) and S.

We determined the ARW kinetics (**Fig. 8**) and the following absolute (g) and relative (%) values of wear of the material of the steel milling tools, i.e. drum (*D*) and balls (*B*), for the systems under study³⁶.

- (i) Fused SiO_2 (3g) and C (1.5g), $\tau=90\text{min}$, *D* (0.63g or 0.077%), *B* (0.52g or 0.5%), ARW = 1.15g.
- (ii) α -quartz (3g) and C (1.5g), $\tau=60\text{min}$, *D* (0.23g or 0.027%), *B* (0.25g or 0.26%), ARW = 0.48g.

Fig. 8 ARW kinetics under MA in an AGO-2 mill of systems: (1) fused quartz-graphite, $0.26 \times \tau^{0.33}$; (2) quartz-graphite, $0.091 \times \tau^{0.37}$; (3) fused quartz-sulfur, $0.005 \times \tau$.

- (iii) Fused SiO_2 (3g) and S (1.6g), 135 min, D (0.21g or 0.028%), B (0.47g or 0.49%), ARW = 0.68 g.
- (iv) Glass (3g) and S (1.6g), 135min, D (0.03g or 0.004%) and B (0.043g or 0.05%), ARW = 0.073g.

We note that the experiment gives higher ARW characteristics for fused silica compared with quartz.

Let us assume that the nanoscale particles formed upon ARW are completely consumed for formation of the phase Fe_3C or FeS_2 by the reaction $3\text{Fe} + \text{C} = \text{Fe}_3\text{C}$ or $\text{Fe} + 2\text{S} = \text{FeS}_2$. Then we would have the following composition of MA products: Fe_3C (1.23g), C (1.42g), and fused quartz (3g); Fe_3C (0.51g), C (1.46 g), and quartz (3g); and FeS_2 (1.46g), S (0.82g), and fused quartz (3g).

3.3 ARW processes caused by the MA of diamond

From the point of view of enhancing the possibilities of the ARW method, the use of diamond is of special interest owing to its unique mechanical and abrasive properties³⁵⁾ and ability to interact with transitional metals and alloys, i.e., a combination of properties of both abrasives and reagents. It should also be noted that mechanochemical synthesis could in the future provide a more efficient utilization of both natural and synthetic diamonds as the result of introducing the low-grade raw material into the technological process. This section is devoted to the study of the influence of the MA of diamond on the synthesis of cohenite $(\text{Fe,Ni})_3\text{C}$, which is a very rare but well-described⁵¹⁾ mineral. It exists in two forms (P_{bnm} , PDF 23-1113; P_{nma} , PDF 35-772). Generally, this mineral has a man-made or extraterrestrial origin³⁵⁾. Its synthetic analogue in the P_{bnm} structure is cement-

Fig. 9 ARW kinetics under MA of systems: (1) copper-diamond-graphite (MA in an EI-2 $\times$ 150mill), $0.23 \times \tau^{0.64}$; (2) diamond charge 2.85 g (MA in an AGO-2), $0.0135 \times \tau$; (3) 1.75g (MA in an AGO-2), $0.0097 \times \tau$.

ite (Fe_3C).

The diamond used in the experiments was obtained in the $(\text{Fe,Ni}) - \text{C}$ system on a multianvil high-pressure split-sphere apparatus at 6 GPa and 1500°C^{52,53)}. Polycrystalline diamond aggregates left as by-products in prolonged experiments⁵³⁾ with the growth of coarse diamond monocrystals are used. The obtained powder, with a particle size of $\sim 0.011\mu\text{m}$, was treated with a heated mixture of nitric and hydrochloric acids to remove impurities. MA of the diamond was conducted in an AGO-2 mill with $N = 400$ for $M = 2.85\text{g}$ and $N = 150$ for $M = 1.75\text{g}$.

We determined the ARW kinetics, see **Fig. 9** (straight lines 2, 3) and **Fig. 10a**, and the next values of wear of the material of milling tools, i.e. drum (D) and balls (B), for the systems under study³⁵⁾:

Fig. 10 XRD patterns illustrating the phase composition: (a) Dynamics of the abrasive wear of the steel milling tools during the diamond MA ($M = 1.75\text{g}$); (b, c) after the diamond MA (1.75g) for 2 h with subsequent annealing for 2 h in the Ar atmosphere at 660 and 960°C, respectively.

Fig. 11 ARW kinetics under MA in an AGO-2 mill: (1) tenorite, $0.53 \times \tau^{0.17}$; (2) galena, $0.0070 \times \tau$.

Fig. 12 ARW under MA of ilmenite in "Mekhanobr" mill: 1(C), $0.038 \times \tau^{0.73}$; 2(B), $0.083 \times \tau$; 3(A), $0.078 \times \tau$.

MA of diamond (2.85g) for 2 h: D 0.42g (0.051%), B 1.20g (1.22%), and ARW(total wear) = 1.62g;
MA of diamond (1.75g) for 2 h: D 0.53g (0.064%), B 0.63g (1.65%), and ARW(total wear) = 1.16g.

Fig. 3a shows a change in the XRD data for the fused quartz-graphite system after the MA. Doublet reflections of diamond at $2\Theta = 43.94^\circ$ and 75.30° (see PDF 75-623) persist during its MA, but their intensity significantly decreases relative to those of the initial sample. The steel milling tools are also worn (Fig. 10a). As can be seen from the XRD patterns of samples of the MA diamond after annealing (Figs. 10 b, c), cementite (see PDF 75-910) is crystallized from the amorphous phase during both the low- and high-temperature annealing. The cementite reflection at $2\Theta = 43.85^\circ$ overlaps the basic reflection of diamond. The inadequacy of the intensity of this line and pres-

ence of the second diamond doublet reflection at $2\Theta = 75.30^\circ$ indicate the presence of residual diamond crystals in the annealed samples. Hence, the MA of diamond can produce the Fe – Fe₃C – diamond composite.

If we admit that the particles produced by the ARW are entirely expended in the generation of the amorphous cementite phase, we would have the following composition of the MA products:

After the MA of diamond: cementite 1.24g and diamond 1.667g (for a diamond sample of 1.75g);
cementite 1.74 g and diamond 2.734 g (for a diamond sample of $M = 2.85$ g).

3.3.1 ARW in copper-diamond-graphite system

The MA of copper-diamond-graphite mix was carried out in an EI – 2×150 milling⁴⁶. Initial weight of the drum $M_d = 953.65$ g, ball charge $M_b = 109.056$ g ($R = 0.2$ cm, $N = 400$). The following powdered sample was subjected to MA (MA time τ varied up to $\tau = 60$ min): diamond (1.3g)-copper (1.3g)- graphite (1.3 g). After the experiment, the weight of the drum was $M_d^* = 952.76$ g, the difference being $M_d - M_d^* = 0.89$ g. The weight of the ball charge was $M_b^* = 106.78$ g the difference being $M_b - M_b^* = 2.27$ g. The total wear of the steel material of the EI – 2×150 milling tools appeared equal $m^* = 0.89 + 2.27 = 3.166$ g, i.e. close to the weight of the initial charge. The ARW kinetics for this system is presented by curve 1 in Fig. 9.

XRD data show that the MA product represents a composite powder containing besides initial components (Cu, diamond, C) of the mix (graphite becomes amorphous and reacts with iron, forming cementite Fe₃C^{35,36}), some nanoparticles of Fe and Fe₃C of ARW. Annealing this product in an argon atmosphere at 600°C and 900°C does not result in the formation of new phases, but rather only the ordering of lattices of mix components. As expected, annealing the MA product during DTA on air up to 1030°C results in the burning-out of carbon and the formation of an appropriate mix of copper and iron oxides.

A specific example of a property of technological relevance that characterizes materials prepared by techniques studied in the present paper is the heat conductivity. Linked to this, the problem of heat removal is very important for the semiconductor industry. For this reason, the improvement of thermal properties of materials used for manufacturing microelectronic components becomes crucial^{30,54}. The "ADS" company offered nanocomposite materials on a Cu and diamond basis that have a higher heat conductivity in comparison with traditionally used

Fig. 13 Process of production (**Picture 1a**) and description of Cu-C sample (**Picture 1b**).

Fig. 14 X-ray phase analysis of the product of mechanical activation of diamond (weight 3g) for 210 min in an EI-2 x 150 mill with Cu fittings.

Fig. 15 TGA of the diamond (1.5g) - graphite (1.5g) system in the atmosphere (210 min, EI-2 x 150 mill).

Fig. 16 Results of processing the XRD data on Cu reflections by the Williamson-Hall method.

Fig. 17 Raman spectrum of the MA copper - diamond - graphite sample. The line of 1334 cm⁻¹ corresponds to diamond.

materials on a Cu or Al basis. Moreover, particles of diamond in copper-diamond composites show a high degree of stability to graphitization under sintering at temperatures up to 1150-1250K, and thus this composite material can be used for the creation of contacts and high-current electric contacts in the low-voltage equipment⁵⁵.

In order to prepare such nanocomposites, the method based on ARW by MA in MRs (with cupric milling tools) using particles of substandard diamonds appears interesting and very able to replace various labor- and power-consuming processes, see **Fig. 13-17** and details in²⁶.

After the MA of diamond and diamond-graphite mixture (1:1), the XRD data virtually did not differ under identical measurement conditions (**Fig. 14**): the MA of both samples does not produce carbon and copper compounds, see also **Fig. 17**. Analysis of MA samples in atmosphere by the DTA method (thermogravimetry - TGA, heating rate 10°C/min) yielded important information (**Fig. 15**). The TGA data can

be used to decipher constituents of composites. For example, based on the TGA, the composite in sample 2 contains 24% carbon (7.3% amorphous carbon and 16.7% diamond). Hence, the Cu content should be 76%, which is very close to the weight analysis data. In order to determine characteristics of the state of copper in the MA powder samples, we processed the XRD data using the Williamson-Hall plot (**Fig. 15**): copper-diamond system ($D_1 \approx 26\text{nm}$, $\varepsilon_1 = 0.43\%$); copper-diamond-graphite system ($D_2 \approx 30\text{nm}$, $\varepsilon_2 = 0.39\%$). Based on the high-resolution SEM data, the relatively large agglomerates of particles have the cauliflower-like internal structure with block dimension similar to certain dimensions of Cu crystallites.

3.4 ARW in abrasive-mineral systems

Recently, a high increase has been observed for the research processing of geological materials in MRs⁵⁶⁻⁵⁸. Of specific interest for extending the potential of the ARW method is also the processing of mineral and technological raw materials^{29,33,37,47,59,60}.

MA of quartz mixes with tenorite (CuO) or galena (PbS) was carried out with the purpose of their reductive processing by iron of the milling tools to obtain copper- or lead-containing composites^{33,59}. Tenorite or galena was introduced in amounts of 1.5 g into a crushed fused silica abrasive in an amount of 3.0g. MA time τ in an AGO-2 mill ($N = 400$) varied from 15 to 210 min. ARW at 60 min in the investigated systems amounted to about 1 g (**Fig. 11**). MA of ilmenite (FeTiO_3) concentrate and its mixes with coke were carried out with the purpose of concentrate reduction to obtain iron and coke, rutile and/or anatase⁵⁸. Conditions of MA in a “Mekhanobr” mill were the following: (A) relation $M_b/M = 2$ at $M_b + M = 166.67 + 83.33 = 250\text{g}$; (B) $M_b/M = 4$, $M_b + M = 200 + 50 = 250\text{g}$; (C) $M_b/(M + M_k) = 4$ at $M_b + M + M_k = 200 + 42.5 + 7.5 = 250\text{g}$, where M_k - weight of coke. MA time varied from 15 to 90 min. ARW curves are shown in **Fig. 12**.

The initial tenorite was obtained by the thermal

decomposition of malachite at $\sim 250^\circ\text{C}$ over the course of 7 h. XRD spectra of this black powder are shown in **Fig. 18a**. The XRD spectrum of the starting sample, based on galena, is shown in **Fig. 19a**. It indicates the presence of not only galena, but also some admixtures (mainly quartz) commonly contained in this mineral. Preliminary experiments demonstrated that the MA involving tenorite and galena shows both similarity and significant differences. In both of the systems, ARW occurs to the steel milling tools, which is more pronounced in the system with galena. Even a short-term (5-15 min) MA of the system with tenorite (**Figs. 11, 18**) results in a self-lining of the milling tools with the material being processed. Tenorite starts to change color to green after 1 h of MA, and this color, as well as the self-lining, is preserved and becomes more intense in the course of MA. By contrast, the self-lining phenomenon is completely absent in the system with galena (**Figs. 11, 19**), and, after a short time of MA, a black homogeneous “oily”

Fig. 18 XRD patterns of the system constituted by fused silica (3g) and tenorite (1.5g). (a) Initial tenorite (cf. PDF 48-1548 and 80-1917); (b) MA duration 60 min; and (c) MA duration 60 min, annealing for 2 h in argon at 700°C (PDF 4-836 for copper).

Fig. 19 XRD patterns of the system constituted by fused silica (3g) and galenite (1.5g). (a) Initial mixture (PDF 1-880); (b) MA duration 60 min (PDF 4-686 and 6-696); (c) MA duration 210 min.

powder of a composite material is formed.

The results obtained in studying the products of MA of the systems under study by XRD and isothermal annealing methods indicate the occurrence of various processes. These are the abrasive wear of steel milling tools, amorphization, and reduction of copper from tenorite and lead from galena. There are no crystalline phases of other products (iron oxides and sulfides) of reduction reactions, e.g. $\text{CuO} + \text{Fe} = \text{Cu} + \text{FeO}$ ($\Delta G^\circ = -28.0 \text{ kcal/mol}$).

Fig. 18b indicates that an X-ray-amorphous product is formed in the system with tenorite and iron wear occurs (peak at $44^\circ\text{--}45^\circ$). The degree of amorphization increases as the processing duration becomes longer, even the Fe peak is broadened. Metallic copper is the only product formed during annealing of this sample at $\sim 700^\circ\text{C}$: reflections of all other products that can be formed in the exchange reaction, namely iron oxides, are completely absent (**Fig. 18c**).

Fig. 19b illustrates a similar phenomenon of abrasive wear of Fe and reduction of galena by this iron, which occurs in this case directly during the course of MA. It should be noted here that there are no reflections of other possible products of the reduction-exchange reaction, namely iron sulfides. If the MA duration is raised to 120 min, the spectrum remains virtually unchanged: only the reflections of the α - SiO_2 admixture in natural galena disappear (because of amorphization). Annealing of these products does not change the situation either: only the relative intensities change insignificantly and the corresponding reflections become considerably narrower. If the MA duration is increased further, abrasive wear of Fe starts to prevail over all other processes (**Fig. 19c**).

The data obtained confirm that the self-lining of milling tools prevents their abrasive wear and, consequently, hinders the reduction reaction of tenorite with the material of milling tools in the course of MA. By contrast, the complete absence of self-lining of milling tools in the system with galena results in a fast breakdown of galena by iron formed in the abrasive wearing of milling tools.

It is difficult to give an unambiguous interpretation of the fact that those reflections of iron oxides or sulfides disappear after the reductive breakdown of tenorite or galena without thoroughly studying the MA of quartz with the material of steel milling tools³³. The results of³³ suggest that the surface of quartz particles can be modified not only by amorphous iron silicates (after annealing of MA tenorite samples), but also by iron sulfides after the MA of ga-

lena together with fused quartz particles. In the case of galena, a nanosize surface layer on quartz particles must be formed of a certain amorphous compound of the system $\text{Fe}_x\text{S}_y - \text{SiO}_2$. An even more complex compound of green color, which is formed upon the MA of tenorite and which contains nanosize particles produced by abrasive wear of the steel accessories (**Fig. 18b**), is the amorphous compound $\text{Cu}_x\text{Fe}_y\text{O}_z - \text{SiO}_2$ on the surface of quartz particles.

The following aspect is associated with dimensional effects. In the case of the conventional MA reduction of, e.g. copper sulfides^{1,28} with metallic Fe powders with an initial particle size of about 0.05 cm, the duration of MA is tens of hours. In the new ARW method of breakdown of, e.g. galena⁵⁹, suggested here, the size of initial particles formed during the abrasive wear of Fe is close to 10 nm (**Fig. 1**), which is several orders of magnitude shorter than that in the conventional mechanochemical exchange reaction. Therefore, the rate of the breakdown reaction involving the material of steel milling tools is also higher and, consequently, the time of the MA breakdown of minerals becomes shorter. The XRD data were used to calculate by the known method^{4,27,61} the structure of crystalline blocks in metal particles obtained in the course of MA in the system with galena. The parameters of the fine crystal structure were calculated from the half width of diffraction peaks (**Figs. 19b, c**) for an MA duration of 60, 210, and 120 min (XRD spectrum is not shown). To determine the instrumental broadening of the lines, we used the profiles of the corresponding reflections after the annealing of these samples. The resulting size of Pb-blocks was (nm): 83 (MA, 60 min), 61 (MA, 120 min), and 46 (MA, 210 min); the corresponding data for particles formed during the wear of Fe were 24, 19, and 12 nm.

Thus, we obtained metal-oxide/sulfide nanocomposite powders based on the quartz matrix in the course of the MA of minerals mixed with an abrasive in an AGO-2 mill with steel accessories.

4. Kinetics and Simulation of ARW

Determination of the ARW kinetic laws of MR milling tools in the MA process of various substances and systems with an abrasive component is of current interest and comes out to the foreground. ARW kinetics was studied by two methods: weight, with an accuracy of measurement of the drum and ball loading weights before and after experiments of not less than 0.01g; volumetric (on hydrogen for diamond-

containing MA products), in reaction of samples with HCl. Data on ARW kinetics in the MA process of the following kinds of mineral raw materials into nanocomposite powders were obtained⁴⁶⁾.

Fig. 2 - quartz (preparation of a magnetic composite^{18,33,34,44,45)}). MA time varied from 5 to 90 minutes. The size of wear at 5 min, ARW in grams, came to 1.43, and at 90 min ARW = 5.14g. The self-lining phenomenon of the surfaces of milling tools by MA quartz is observed.

Fig. 8 - mixes of quartz and fused quartz with graphite or sulfur (preparation of cementite- or pyrite-bearing composites^{36,38)}). MA of the system with graphite results in a self-lining of the milling tools. By contrast, the self-lining phenomenon is completely absent in the system with sulfur.

Fig. 9 - diamond (to obtain cohenite³⁵⁾) and a powder mix of diamond, graphite, and copper (to obtain high-heat-conducting composite materials^{26,30)}). During diamond MA, a self-lining of the milling tools is barely visible. During the mix MA, the self-lining takes place.

Fig. 11 - mixes of fused quartz with tenorite or galena (preparation of copper- or lead-bearing composites^{1,14,15,33,59)}). MA of the system with tenorite results in a self-lining of the milling tools. By contrast, the self-lining phenomenon is completely absent in the system with galena.

Fig. 12 - ilmenite concentrate of the arm filters of titanium-magnesium manufacture and mixes of concentrate with coke (for reduction of concentrate to obtain iron, rutile and anatase⁶⁰⁾). The appreciable self-lining of milling tools' surfaces by MA materials was only observed in case (C).

The linear law of ARW growth with MA time τ in the absence of a self-lining phenomenon is established and the ARW power law in the presence of the self-lining with an exponent less than unity. Mathematical processing of measured ARW(τ) values in various mills and MA systems gives the following empirical dependence: $ARW(g) = K \times \tau^n$, where K is a rate constant of ARW, and n is an exponent⁴⁶⁾. We see that both a rate constant (K , from 0.0050g/min for MA system sulfur-fused quartz up to 1.8g/min^{0.23} for quartz MA) and an exponent (n , from 0.17 for MA tenorite up to 1 for systems in which the self-lining does not take place) vary in sufficiently wide numerical intervals. It is evident from an example of the MA of diamond and ilmenite that K depends on the MA conditions ($n = 1$). For diamond $K = 0.0135$ g/min at $M = 2.85$ g and number of balls $N = 400$, $K = 0.0097$ g/min at $M = 1.75$ g and $N = 150$. For ilmenite $K =$

0.0078g/min at $M/M_b = 0.5$, and $K = 0.0083$ g/min at $M/M_b = 0.25$.

Under identical MA conditions, the K and n values essentially depend not only on the specificity of chemical reactions but also on a phase state of an abrasive. For tenorite $K = 0.53$ g/min and $n = 0.17$, for galena $K = 0.007$ g/min and $n = 1$. For a mix of graphite with quartz $K = 0.091$ g/min and $n = 0.37$, for a mix of graphite with fused quartz $K = 0.26$ g/min ^{n} and $n = 0.33$. For a mix of sulfur with fused quartz $K = 0.005$ g/min ^{n} and $n = 1$.

As regards the problem of ARW simulation, in our opinion, it is necessary to discuss the approaches to this problem recently proposed in^{48,62)}. In these works, the authors considered the athermic (diffusion⁴⁸⁾ and deformation⁶²⁾ mechanisms of the formation of cementite (Fe_3C) upon MA of an iron and carbon powder mixture. Note that the role of local heating due to the impact-friction interactions in the course of MA²⁾ was ignored completely. This contradicts the practice of mankind³⁶⁾ throughout the ages, which has been aimed either at decreasing the heating of materials upon their mechanical treatment or at using a released heat, including the primitive ways of making fire. The modeling of the MA process associated with the development of short pressure or temperature pulses or the so-called t - P - T conditions^{2,3,7)} is based on the rigorous thermodynamic basis. In our opinion, this basis can be complemented by invoking diffusion and deformation processes, but cannot under any circumstances be replaced by them. Details of ARW simulation with the account of the t - P - T conditions both on contact with the treated particles and on contact with the milling tools are given in^{12,34-36,42,61)}.

5. Conclusion

The study performed demonstrated that the steel material of milling tools can be involved in a direct breakdown of minerals and synthesis of nanocomposites under utilization of the abrasive properties of diamond and different boron and quartz modifications. The chemical interaction between the material of milling tools and the substance being processed was simulated numerically for the example of quartz processing in a planetary ball mill. It was shown that quartz processing resulted in the synthesis of iron silicates from silica and iron oxides. Nanoscale iron and iron oxide particles were formed as a result of the abrasive-reactive wear of steel mill fittings by quartz particles. The estimated thickness of the layer

of silicates on the surface of quartz particles was ~2 nm. The mechanical activation of mixtures of quartz (or diamond) and reagents (copper, graphite, sulfur, tenorite and galena) yielded nanocomposites in a time one to two orders of magnitude shorter than that in the case of the mechanical activation of mixtures of iron powders with the reagents. We have substantiated a new field of low-grade diamond utilization, namely an abrasive-reactive synthesis based on the material of the milling tools of mechanochemical reactors. A scrap of any metal and ceramic product can be used as milling tools, which makes it possible to considerably extend the potential of the abrasive-reactive wear method and the range of treated compounds. The kinetics and mechanism of abrasive-reactive wear of steel milling tools in the planetary mills were investigated experimentally and modeled numerically under defined conditions of mechanical activation.

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