Fracture, Grinding, Mechanical Activation and Synthesis Processes in Solids Under Mechanical Action

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Abstract:
The parameters of mechanical action on solids were determined for apatite and quartz as examples, providing separation between fracture, grinding and mechanical activation processes in solids. The texture, structural and chemical changes accompanying these processes in the samples under investigation are shown. The data on mechanochemical synthesis of isomorphous apatite modifications in multicomponent systems are reported. A reversible character of mechanochemical activation and mechanochemical synthesis is discovered.

Keywords: Fracture, grinding, mechanical activation, apatite, quartz.

Introduction

Diverse processes are observed during mechanical action on solids. Depending on the conditions of mechanical treatment and the properties of solids, processes such as plastic deformation, fracture, grinding, mechanical activation accompanied by structural and chemical transformations can take place, and in multicomponent systems mechanochemical synthesis can also occur. Each of these processes is determined by the level and amount of energy input during mechanical treatment and the stability of the lattice of a solid to mechanical action. In spite of interconnectione between processes, for example, interaction between dislocations, which can be accompanied by the formation of cracks, and plastic flow which can lead to fracture, the level of mechanical strain necessary for one or another process in a solid should be taken into account. In some research [1, 2], mechanical activation of solids is explained by the accumulation of a large number of defects. However, in order to carry out mechanical activation, the intensity of mechanical action should be several orders of magnitude higher than that at the initial stage of plastic deformation, when the movement of dislocations starts, and higher than for grinding. The dependence of processes occurring under mechanical action on the strain arising in the solid can be represented by a qualitative diagram in the coordinates "strain – process" built up on the basis of the data for apatite as shown in

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Fig. 1 [3]. The zone of plastic deformation (Fig. 1, zone 2) characterized by the level of strain causing the deformation lies lower than the zone of the fracture process, which lies an order of magnitude lower than the zone of the initial stage of mechanical activation (zone 6).

When the strain equal to the breaking point of a single crystal is achieved ($\sigma_\circ \sim 0.1$ GPa), its fracture will start (zone 4 in Fig. 1). As particle size decreases, an increase in the imposed load is required for further grinding. Particles of a "critical" size are the limit of grinding (region 5). At the strain exceeding the theoretical ultimate strength ($\sigma_y$) of a solid ($\sim 1.78$ GPa for apatite and $1.26$ GPa for quartz), the lattice loses its stability, and the structure is transformed, that is, mechanical activation of the substance occurs (zone 6) [3].

In the present work we describe the results of investigations of these processes on the example of isomorphous modifications of apatite and quartz.

**Experimental**

Fracture processes were investigated in natural apatite with different qualitative compositions of isomorphous admixtures and paramagnetic centers (PMC) localized in different lattice positions. The chemical composition of the samples is shown in Table I, (samples No. 1-4). Distortions of short-range ordering in various fragments of apatite structure were observed by recording changes in the intensity of ESR spectra [4]. The ESR spectra were recorded with a standard RE 1306 spectrometer ($\lambda=3$) at room temperature. At the same time, distortions of the long-range order were determined on the basis of changes in the crystallinity degree of the samples as exhibited by the data of X-ray structural analysis for the characteristic reflections of apatite. X-ray diffraction studies of the samples were carried out with a DRON-3 instrument using Cu $K_\alpha$ radiation with a Ni filter. The crystallinity degree was determined using equation: $K = (I_{act}/I_{init}) \times 100\%$, where $I_{act}$ and $I_{init}$ are intensities of X-ray lines of the activated and initial samples, respectively [5]. Crystallinity of the initial sample was conventionally accepted to be 100%. The value of $K$ was calculated for the apatite characteristic reflections from the planes with $d$-spacing: (0002) – 0.344 nm, (12 $\overline{3}$ 1) – 0.279 nm; (30 $\overline{3}$ 0) – 0.269 nm (12 $\overline{3}$ 1) – 0.279 nm, (30 $\overline{3}$ 0) – 0.269 nm, (20 $\overline{2}$ 2) – 0.261 nm.
The subjects, on which the grinding process and mechanical activation were investigated, were samples of the Khibin apatite concentrate – sample No. 5 (Table 1) and natural quartz from the Slyudyanka deposit – sample in Table 2.

Mechanochemical synthesis of isomorphous modifications of apatite was carried out using analytically pure grade reagents; the reagents were salts and oxides in the solid state. IR spectra were recorded with a Specord-75 DR device. The samples were pressed as tablets with dried KBr.

Electron microscopic studies were carried out with a JSM-T20 scanning microscope (SEM), and with a JEM-100CX transmission microscope (HRTEM) [6, 7]. The samples for SEM were sprayed with gold; for TEM, the samples were sprayed with the help of a supersonic set-up onto perforated carbon substrates in the form of a suspension in ethanol.
Tab. III. The chemical-physical properties of natural apatite (№ 5, table 1) depending on the mechanical activation conditions

<table>
<thead>
<tr>
<th>Sample №</th>
<th>The samples and mechanical activation condition characteristics</th>
<th>Activation time, min</th>
<th>Specific surface, m²/g</th>
<th>Sample density x10⁻³ kg/m³</th>
<th>The contest of P₂O₅ ammonia citrate (pH=9) solubility, relative %</th>
<th>“Excess enthalpy” ΔH kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial</td>
<td>0</td>
<td>0,5</td>
<td>3,15</td>
<td>not detected</td>
<td>not detected</td>
</tr>
<tr>
<td>2</td>
<td>Sample №1 activated in water</td>
<td>40</td>
<td>50,3</td>
<td>3,14</td>
<td>9,7</td>
<td>not detected</td>
</tr>
<tr>
<td>3</td>
<td>Sample №2 in air condition, by d = 8 mm ball</td>
<td>60</td>
<td>4,1</td>
<td>3,08</td>
<td>29,8</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Sample №2 in air condition, by d = 3 mm ball</td>
<td>60</td>
<td>3,7</td>
<td>3,27</td>
<td>98,1</td>
<td>122</td>
</tr>
<tr>
<td>5</td>
<td>Sample №1 in air condition, by d = 3 mm ball</td>
<td>60</td>
<td>4,2</td>
<td>3,24</td>
<td>50,3</td>
<td>64</td>
</tr>
</tbody>
</table>

Mechanical activation of the samples was carried out in an EI-2×150 laboratory planetary mill with a drum rotation frequency of 850 RPM. The mill has two drums, with a volume of 150 cm³ each. For ESR examination, apatite samples (№ 1-4, see Table I) with a mass of 3 g were activated in the drums lined with ceramics, by ceramic balls 5 mm in diameter, with a total mass of 100 g per each drum. For investigations by other methods, the apatite (№5, Table I and Table III) and quartz samples (Table II) were activated in steel drums with steel balls 3 and 8 mm in diameter, the ball load for each drum being 200 g per drum; weighed portions of the substance under treatment were 3 to 10 g.

Results and Discussion

Fracture processes of the short- and long-range structure order

Fragments of the initial matrix in definite crystallographic directions can be conserved on anisotropic crystalline samples under mechanical action, while in other directions the long-range and even short-range order can be distorted. Isomorphous apatite modifications are an interesting subject to investigate this process. Substitutions of anions and cations localized in different structural fragments of apatite provide lattice regions less stable to mechanical action. In natural apatite, Mn²⁺ substitutes the position of Ca²⁺ cations along the C₃ axis. Complexes with PMC like F⁻ - O⁻ - F⁻, F⁻ - O⁻ - Cl⁻; Cl⁻ - O⁻ - Cl⁻ are localized on the 6₃ axis, while PO₄³⁻ and SO₄²⁻ paramagnetic centers are localized in the positions of the PO₄³⁻ tetrahedron in the apatite structure [8].

Similar substitutions and PMC were present in apatite samples from different deposits investigated by us (Table I). Distortions in the short-range order of separate fragments in the
apatite structure were traced by the changes in the intensity of the ESR spectrum during mechanical activation [4]. At the same time, distortions of the long-range order were determined from the changes in crystallinity of the samples as exhibited by the data of X-ray phase analysis for the characteristic reflections of apatite. Depending on the localization of isomorphous impurities, different stability of the structure of apatite samples in the same crystallographic planes was revealed. According to ESR data, the short-range order in the coordination surroundings of calcium ions occupying the first position gets distorted, which is observed as a decrease in the intensity of the spectrum of Mn$^{2+}$, which substitutes Ca$^{2+}$ (Fig. 2,a). In apatite samples with an insignificant chlorine content (Table I, samples 1 and 2), a decrease in crystallinity calculated from a decrease in the intensity of reflections from (0002) planes corresponded to the curves of relative intensity for F'-O' - F PMC (Fig.3, a and 2, b, curves 1 and 2). This is evidence of structural distortions in the apatite lattice in planes parallel to the basis plane, with the rupture of F'-O'-F bonds. At the same time, crystallinity of the fluorchlorapatite sample (Table I, sample 4) decreased sharply within the first minute of activation (Fig. 3, a, curve 4), with insignificant changes in the intensity of F'-O' - F' PMC (Fig. 2,b and c, curve 4). It may be assumed from these data that the fracture of the structure occurs first of all in the most strained fragments of the basis plane where chlorine ions are localized.

![Fig. 2 ESP-spectra intensity of PMC versus activation time of apatite: a) Mn$^{2+}$→Ca$^{2+}$; b,c) F'-O' - F, F'-O' -Cl, Cl' - O' - Cl'; d) PO$_3^{2-}$, curve numbers correspond to sample numbers in table 1 [4]](image)

Changes in the intensity of the ESR spectrum of the electron-type paramagnetic center PO$_3^{2-}$ during mechanical activation of the samples differing in composition were ambiguous. Within
five minutes of apatite activation (Table I, sample 2), the intensity of ESR spectrum of $\text{PO}_3^{2-}$ PMC increases (Fig. 2, d, curve 2), possibly due to electron capture by the $\text{PO}_3^-$ fragment according to the scheme: $\text{PO}_3^- + e^- \rightarrow \text{PO}_3^{2-}$ [8], which is an evidence of electron transfer induced by mechanical action. In this sample, we observed a correlation between the dynamics of the ESR spectrum of $\text{PO}_3^{2-}$ with the changes in sample crystallinity as evidenced by the reflections from $(30\bar{3}0)$ planes (Fig. 3, b, curve 2). It is these planes of the apatite lattice where the oxygen atoms $\text{O}_{\text{III}}$ are located; their shift causes the formation of $\text{PO}_3^-$ fragments.

Results of the investigation of natural apatite demonstrated that structural imperfection of the samples with isomorphous substitutions has a substantial effect on the stability of the structure to mechanical action. This is clearly observed during the first minutes of activation. For longer treatment, fracture occurs along the planes in a sequence corresponding to the predominance of sliding, which is typical for the crystals of this syngony.

![Fig. 3](image)

**Fig. 3** Variation of the apatite crystallinity ($K$) degree depending on the activation time: (a) - reflex (0002) and (b) reflex (30 $\bar{3}$ 0). The samples numbers are - in the tab. I

![Fig. 4](image)

**Fig. 4** (a) -XRD pattern of mechanically activated quartz; (activation time in the planetary mill 60 min); (b) - IR-spectra of quartz: 1 – initial, 2 – activated 30 min, 3 – activated 60 min.

Quartz is one of the common subjects on which fracture and activation of solids are investigated [9-12]. We investigated natural quartz samples containing 99 % $\text{SiO}_2$ (Table II).
Mechanical activation of quartz in the planetary mill was accompanied by amorphous phase formation [3]. A non-trivial fact was observed: according to the data of IR spectroscopy, the distortion of the short-range order occurs under activation in quartz with the conservation of one of the \(d\)-spacings of the primary matrix (Fig. 4, a). As the time of mechanical treatment increased, the number of absorption bands of Si – O bond vibrations decreased (Fig. 4, b). After activation for 60 min, the IR spectrum of the sample contained only three broad absorption bands typical for amorphous SiO\(_2\). At the same time, an intensive reflection with the \(d\)-spacing of 0.334 nm - reflection from (10\(\bar{1}\)0) was present in the diffraction patterns (Fig. 4, a). The transition of quartz into the amorphous and a polymer-like state during activation occurs with the participation of water steam which is present in the air in the mill. The density of samples decreased from 2.70.10\(^3\) kg/m\(^3\) to 2.40.10\(^3\) kg/m\(^3\) (Table II). So, similar to mechanical activation of apatite, local destruction of the quartz structure is observed.

**Grinding and aggregation processes**

Grinding processes have been investigated for nearly two centuries; thousands of papers describe these investigations. A number of theories have been proposed for determining energy consumption for an increase in the surface area and/or decrease in particle size, different types of grinding devices have been evaluated; an overview of some data was presented in monographs and reviews [13-21]. Models have been developed for grinding processes involving the free crushing method [16]. Successful investigations were carried out by German researchers using an "individual grain" procedure [17-21]. In some cases grinding is complicated by the aggregation of particles [14, 22]. The author of [20, 23] proposed a two-step grinding process: crushing by pressing until a partial particle agglomerate is obtained, followed by desaggregation, which allows one to decrease energy consumption by tens per cent in comparison with the usual grinding procedure in a ball mill. In spite of efforts of many years and numerous publications dealing with fracture and grinding processes, the investigation of these processes is far from being completed.

In the present section, we will present only some examples of grinding and aggregation during the activation of apatite, quartz, calcite and their mixtures.

It is known that grinding proceeds with higher efficiency in the presence of water and the size of resulting particles is smaller than that for dry grinding [14]. Apatite exhibits very low solubility in water, its constant K - solubility product at 298K is \(K = 100^{115}\) [24]. This allowed us to separate grinding and activation processes. After mechanical treatment of the aqueous suspension Khibin apatite concentrate (solid to liquid ratio \(S : L = 3 : 25\)) for 40 minutes, the specific surface of the sample increased from 0.5 m\(^2\)/g to 50.3 m\(^2\)/g (Table III, sample 2), and particle size was 5 to 50 nm; the extended lattice was conserved (Fig. 5, a). However, in spite of low solubility of apatite, its activation for longer time in water in a planetary activator was likely to be accompanied by its partial recrystallization, because the surface of particles was coated with small crystals (Fig. 5, b).

An apatite sample ground in water (Fig. 5, a) was annealed at 673K, and activated once more in the planetary mill in air. The particles were not ground but a strong plastic flow occurred, accompanied by particle aggregation (Fig. 5, c).

Changes in the properties of the substance depended on the diameter of milling balls (Table 3). With balls 8 mm in diameter, the specific surface of apatite sample ground preliminarily in water decreased from 50.3 m\(^2\)/g to 4.1 m\(^2\)/g, and with balls 3 mm in diameter, down to 3.7 m\(^2\)/g. Physicochemical properties of the substance changed in different manners, too. After treatment with balls 8 mm in diameter, the density of the sample decreased from 3.14.10\(^{-3}\) kg/cm\(^3\) to 3.08.10\(^{-3}\) kg/cm\(^3\), while with balls 3 mm in diameter, quite contrary, the
density of the sample increased up to $3.27 \times 10^{-3}$ kg/cm$^3$. The particles of this sample were dense aggregates and most particles were in the amorphous state (Fig. 5, c). The solubility of the samples in ammonium citrate (pH=9), which is a test to determine the suitability of apatite as a fertilizer [25], and the amount of accumulated energy, the so-called “excess enthalpy”, were also different (Table III).

These results can be explained by different relations and intensities of impact-attrition loads depending on the diameter of balls used in the activator, so that structural and phase transformations of the substance can occur in the compression or off-loading wave [3].

The grinding degree and changes in the specific surface depend on physical and mechanical properties of the substance. This is clearly exhibited for the mechanical treatment of quartz, calcite, apatite minerals and their mixtures, in a planetary mill. At the first moment of treatment, the curves of the growth of specific surface were affine for each of these
minerals (Fig. 6). After apatite grinding for 5 min, a decrease in its specific surface occurs (Fig. 6, curve 1).

An increase in the specific surface of quartz is proportional to the treatment time (Fig. 6, curve 2), while for calcite, an increase in the specific surface almost stopped after treatment for 20 minutes (Fig. 6, curve 3). Mechanical activation of a mixture of these minerals was accompanied by aggregation and reduction of the specific surface (Fig. 6, curve 4).

Mechanochemical synthesis and mechanical activation as reversible processes

Mechanical activation of fluorapatite causes its transformation into the amorphous phase with spherical particles; nano-particles of tricalcium phosphate $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ are crystallized from them during aging (Fig. 7).

Because of this, mechanical activation of fluorapatite can be represented as a decomposition according to the equation
Mechanical activation

\[ \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \leftrightarrow 3 \text{Ca}_3(\text{PO}_4)_2 + \text{CaF}_2 \]

Mechanochemical synthesis

At the same time, mechanochemical synthesis of fluorapatite from triple-substituted calcium orthophosphate (TCP) and fluorite CaF\(_2\) can be represented as a reverse reaction. The kinetics of these opposite processes was followed by observing changes in the solubility of the synthetic mixture and natural fluorapatite in a 2% citric acid solution, depending on the treatment time (Fig. 8). During mechanical activation of natural fluorapatite, its solubility in a 2% citric acid solution increases gradually till 120 min of treatment (Fig. 8, curve 2). An increase in the activation time to 180 minutes is accompanied by a decrease in the solubility, which means that a reverse process starts: the synthesis of fluorapatite.

![Fig. 8](image)

**Fig. 8** Solubility of P\(_2\)O\(_5\) (relative to the total content) in a 2% citric acid solution (\(\alpha\)): mixture \(3\text{Ca}_3(\text{PO}_4)_2 + \text{CaF}\) (1), and natural fluorapatite (2), depending on the activation time

The solubility of fluorapatite is much lower than that of TCP, and a decrease in the solubility of the synthetic mixture during mechanochemical interaction is evidence of the formation of fluorapatite (Fig. 8, curve 1). This is confirmed by the data of X-ray phase analysis of the reaction mixture at different stages of synthesis (Fig. 9). The diffraction patterns become most intensive after activation of the synthetic mixture for 120 minutes (Fig. 9, pattern 5). An increase in the mixture activation time up to 180 minutes causes partial amorphization of the formed product (Fig. 9, patterns 6).

The mechanochemically synthesized apatite with substitutions, similarly to natural apatite listed above (Table 1, samples 1-4) is less stable to mechanical action than simple fluorapatite. We synthesized francolite, which is most widespread among the natural sedimentary minerals [26], by mechanochemical method from the reaction mixture according to the reaction:

\[
2,5 \text{Ca(H}_2\text{PO}_4)_2\text{H}_2\text{O} + 0,13\text{Na}_2\text{CO}_3 + 0,1 \text{MgO} + 1,25 \text{CaF}_2 + 0,87 \text{CaCO}_3 + 5,02 \text{CaO} \rightarrow \text{Ca}_{9,64}\text{Na}_{0,26}\text{Mg}_{0,1}(\text{PO}_4)_3\text{CO}_3\text{F}_{2,5}(\text{OH})_{0,24}
\]

The presence of sodium compounds accelerates the interaction between the
components of the mixture; after activation for 20 min, crystalline francolite is formed directly in the planetary mill, as identified by means of X-ray phase analysis and IR spectroscopy (Fig. 10, spectrum 1).

Further activation of the mixture leads to destruction of the structure, which is exhibited as a disappearance of a number of absorption bands from the IR spectrum, that is, partial amorphization of the obtained product occurs (Fig. 10, spectrum 2). The same kinetics was observed under mechanochemical synthesis of sulfate fluorapatite according to the reaction:

$$3 \text{Na}_2\text{SO}_4 + 3 \text{CaSO}_4.2\text{H}_2\text{O} + \text{CaF}_2 \rightarrow \text{Na}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2$$

After activation of the mixture for 20 min, crystalline sulfate apatite formed directly in the mill (Fig. 10, spectrum 3). An increase in the time of activation to 40 minutes caused the destruction of synthesized apatite (Fig. 10, spectrum 4).

So, the structure of synthetic apatite with substitutions creating strain in the lattice is less stable to mechanical action, and the reverse process, that is, its destruction occurs after treatment for a shorter time. An example may be comparison between the kinetics of the processes:

- «mechanochemical synthesis ↔ activation» of fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and francolite $\rightarrow \text{Ca}_{9.64}\text{Na}_{0.26}\text{Mg}_{0.1}(\text{PO}_4)_5\text{CO}_3\text{F}_{2.5}(\text{OH})_{0.24}$. 
Conclusions

1) The effect of mechanical treatment on fracture and transformation of the crystal structure of solids is investigated on apatite and natural quartz as examples. Local destruction of the lattice of these compounds is revealed. In isomorphous modifications of apatite, the fracture starts in fragments where the ions substituting calcium, phosphate and fluorine are localized, creating strained regions in the lattice. Under the activation of quartz in a planetary apparatus, the long-range order is conserved in the planes parallel to (1010) (most stable to mechanical action); at the same time, as suggested by the IR spectroscopic data, the short-range order of the structure is destroyed.

2) Apatite grinding in an aqueous suspension allows obtaining of nano-particles with an extended lattice. The subsequent mechanical activation of these samples in air is accompanied by strong aggregation due to the plastic yielding of apatite. For the mixture of apatite, quartz and calcite as an example, the mutual influence of the minerals on grinding and aggregation processes is demonstrated.

3) By means of mechanochemical methods, using salts and oxides in the solid state as initial compounds, apatite with a complicated composition were synthesized: francolite $\text{Ca}_{9.64}\text{Na}_{0.26}\text{Mg}_{0.1}(\text{PO}_4)_5\text{CO}_3\text{F}_{2.5}(\text{OH})_{0.24}$, fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and sulfate apatite $\text{Na}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2$. Reversibility of mechanochemical synthesis and activation of the isomorphous modifications of apatite is demonstrated. The kinetics of the direct and inverse processes is determined by chemical composition and the stability of structure to mechanical action.

4) Depending on the conditions of mechanical activation and phase transformations that take place, the density of apatite either increases up to $3.27 \times 10^{-3} \text{ kg/cm}^3$ or decreases to $3.08 \times 10^{-3} \text{ kg/cm}^3$, its initial density being $3.14 \times 10^{-3} \text{ kg/cm}^3$. During activation, quartz interacts with water vapour present in the air inside the mill, and its density decreases from $2.70 \times 10^{-3} \text{ kg/cm}^3$ to $2.40 \times 10^{-3} \text{ kg/cm}^3$. Changes in the density of minerals during mechanical activation can be explained by transformation of the structure in the compression or off-loading wave during mechanical treatment.

References

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Резюме: Определены параметры механических воздействий, разделяющие процессы разрушения, измельчения и механической активации на примере минералов апатита и кварца. Выявлены текстурные, структурные и химические преобразования в исследованных образцах, сопровождающие эти процессы. Приведены данные механохимического синтеза изоморфных разновидностей апатита в многокомпонентных системах. Выявлен обратимый характер процессов механической активации и механохимического синтеза.

Ключевые слова: Разрушение, измельчение, механическая активация, апатит, кварц.

Садржај: На примеру апатита и кварца одређени су параметри механичке активације чврстих тела који раздвајају процесе фрактуре, млевења и механичке активације. За проучене узорке приказане су текстурне, структурне и хемијске трансформације које прате ове процесе. Дати су подаци о механохемијској синтези изоморфних модификација апатита у вишекомпонентним системима. Откривен је реверзилбилин характер механихемијске активације и механохемијске синтезе.

Кључне речи: Фрактура, млевење, механичка активација, апатит, кварц.