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Review

Efficiency and Prospects of the Use of Mechanochemical Treatment to Obtain Innovative Composite Systems

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Abstract: This review is devoted to the possibilities of using mechanochemical processing and to achievements in this field for obtaining materials for a wide range of purposes. The mechanochemical processing of various materials and compositions in energy-intensive grinding devices allows the production of innovative systems, ensuring the necessary complex structure and properties. A detailed analysis of the processes of mechanochemical processing in the production of designs for various purposes is given, and the latest practical results in this area are highlighted. A detailed analysis of the processes of mechanochemical processing in the production of structures for various purposes is given, as well as recent practical results in this area, such as the use of mechanochemical processing to increase the performance of aluminum and other metals used as a combustible substance in energy-intensive systems. This review also presents the prospects for the use of mechanochemical processing to obtain physiologically active drugs from plant materials, which is an effective method for creating new materials in the field of pharmaceuticals, animal husbandry, veterinary medicine, crop production, etc.

Keywords: mechanochemical treatment; grinding; modification; composite materials

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1. Introduction

Mechanochemical processing of organic and inorganic materials using energy-intensive grinding devices is currently one of the innovative methods for obtaining new materials, with desirable properties for various functional purposes (energy-intensive systems, catalysts, sorbents, building materials, etc.) [1,2]. During mechanochemical treatment (MCT), in addition to the dispersion of particles, the following occurs: deformation of crystals, formation of a large number of defects, changes in the size of micro blocks forming a crystal, shear stresses, aggregation of crystallites, heat release, a local rise in temperature and pressure, emission of light and electrons, phase transformations, amorphization and breaking of chemical bonds, acceleration of diffusion processes, and formation of centers with increased activity on newly formed surfaces [3,4]. All these processes provide an increase in the activity of processed solids as a result of the occurrence of vibrationally and electronically excited states of interatomic bonds, as well as mechanically stressed and broken bonds, including the presence of free radicals, coordinatively unsaturated atoms, various structural defects, the ionization of particles of matter, and stabilization of electrically charged centers [5–7]. All structural changes result from the absorption of mechanical energy by the substance during automated processing, which leads to its activation [8]. Such a system with a developed defect structure and accumulated excess free energy is not in thermodynamic equilibrium, providing it with an increased reactivity.

Identifying specific factors responsible for the increase in reactivity is one of the most critical tasks in studying the physicochemical properties of mechanically activated

substances. The increased activity (reactivity) of various materials after MCT is used in subsequent processes for the practical application of treated systems (sintering, synthesis, combustion, catalysis, sorption processes, dissolution, etc.). MCT is used to accelerate technological processes or as a way to change the technical parameters of the processing mode of various mineral raw materials. During mechanochemical treatment of metal particles, the concentration of dislocations increases. As a result, the thermokinetic characteristics of the combustion process are also intensified. From the obtained thermograms, it follows that after the MCT of the mixture, the induction period of ignition decreases and the combustion temperature of the thermite mixture increases [9]. A general scheme for the use of mechanochemical processing in modern technological processes, according to the results of work in [10], is shown in Figure 1.

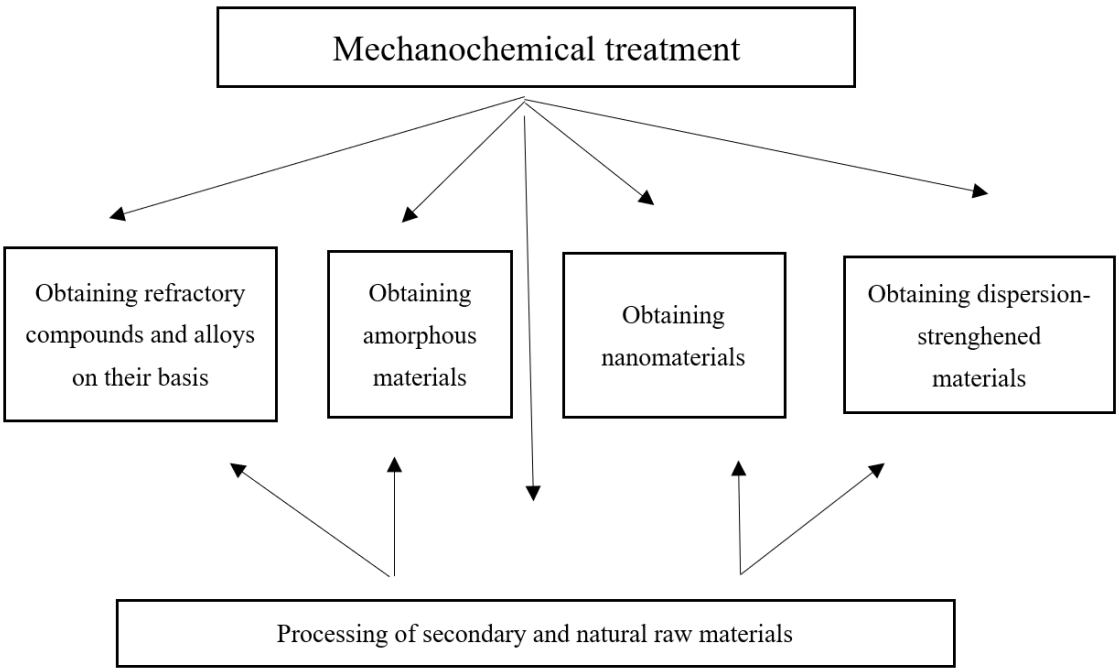


Figure 1. Application of mechanochemical technology in modern materials science [10].

At the same time, the energy costs for activation are paid off by saving time and energy costs in the subsequent technological processes, particularly in self-propagating high-temperature synthesis (SHS) [11].

The importance of using MCT in the processing of various solid materials lies in the ability to control the formation of the structure (nanoarchitecture), the creation of active centers, and control of the chemistry of the surface layer of particles, determining their reactivity and the functional direction of their subsequent use. To control such tasks during MCT, in most cases, processing of the mixture, i.e., processing of inorganic and organic substances, is carried out simultaneously [2], thus ensuring the modification of the surface the crushed materials [12,13]. Acceleration of chemical reactions between organic and inorganic substances during MCT is mainly due to electrification of the character in the places of where splitting and cracks of the solid particles occurs, which are a kind of micro capacitor, with high electric fields reaching 107 V cm^{-1}. Electrons in such areas are accelerated to high speeds, causing polymerization of the organic compounds in the treated mixture and their grafting to the newly formed surface of the solid inorganic particles, i.e., their modification [14,15].

When processing metal plastic powders under the conditions of mechanochemical action (i.e., the simultaneous mechanical action of the tool and a chemically active medium), facilitation of the initiation and development of microcracks in the oxidized metal layer takes place. In this case, with the simultaneous modification of the surface with organic

compounds, it is possible to significantly accelerate the chemical reactions of the treated metal particles with other substances; for example, when creating various metal–ceramic compositions [16].

To increase the efficiency of grinding viscoelastic plastic bodies and metals, various surface-active substances (surfactants) are used. The use of liquid surfactants does not entirely eliminate the oxidation of the material being ground, due to the heating of the mixture to 60–80 °C and higher during MCT and the presence of water and oxygen dissolved in the surfactant, as well as the air present in the working space of the grinding equipment. As mechanically destructible organic substances that facilitate metal dispersion, in most cases, solid-phase high-molecular compounds are used, which undergo mechanical destruction under the mechanical action [17].

The products of the mechanical destruction of a high-molecular compound penetrate the surface microcracks, and polymerization processes begin to occur on their faces, with the formation of a high-molecular product, thus leading to a sharp increase in stresses in the dead-end region of the microcracks and advancement of the crack front into the depths of the metal. The kinetics of crack development is determined by the rate of mechanochemical processes and the concentration of mechano- and thermal destruction products. Polymethyl methacrylate, characterized by a deficiency of bound oxygen, is used as a high molecular medium capable of undergoing mechanical destruction and generating low molecularly active components. The products of polymethyl methacrylate mechanocracking penetrate into the surface cracks, forming thin films on the faces and preventing their closing [17]. Thus, when processing a mixture of magnesium with fluorine-chloropolymers (fluoroplast), a film is formed on the surface of metal particles, due to an increased concentration of active particles of fluoroplast macroradicals during MCT [18,19]. In this case, two types of radicals are possible: macroradicals formed upon rupture of polymer molecules, and peroxide macroradicals, which are adsorbed on the surface of metal particles. When a polymer film is formed on the surface of the particles, the composition is a mixture, with a high contact surface of the reagents. All this ensures the high reactivity of the mix of metal and fluoroplastics. Consequently, a high rate of transformation over a wide concentration range can contribute to a change in the explosive properties of such composites consisting of a metal and fluoroplast [20].

2. Features of the Structure and Properties of Energy-Intensive Metal Compositions Obtained by Mechanochemical Processing

If the last century was the time of the formation of mechanochemistry as an independent scientific field of controlling the structure and properties of solid-phase systems, a method of accelerating chemical and physicochemical transformations, the 21st century has been the time of expanding the practical implementation of theoretical developments on the reactivity of matter after MCT. At first, attention was paid to the MCT of non-metallic systems for obtaining various ceramic compositions [3,21,22]. Currently, more and more attention is being paid to using MCT to obtain energy-intensive combustible pieces for multiple purposes, especially for rocket engines. In such systems, a significant role is assigned to metallic fuels. These include aluminum, magnesium, zinc, zirconium, boron, beryllium, lithium, and their hydrates and alloys. As a rule, these are used in mixed solid fuels (MSF). The metal in the fuel composition is an energy additive that increases the heat output, specific impulse, and fuel combustion rate [23].

Each of the metal additives has its specific manner of changing the quality of fuel mixtures. Adding zirconium leads to a high fuel density but reduces the specific thrust. From a safety point of view, boron does not cause any difficulties, while aluminum and magnesium have a low flammability, and lithium and zirconium are the most explosive; when working with beryllium, special measures must be taken due to its toxicity.

In addition, metal additives increase the specific gravity of the fuel, which improves the characteristics of the engine and the rocket as a whole [24]. It should be taken into account

that the higher the content of metal-containing fuel, the higher the temperature of their combustion products. Almost all modern composite fuels contain metals as components.

The most widely used and cheapest metal fuel is aluminum. Due to the high heat of combustion ($\Delta H = -837.5$ kJ/mol), powdered metallic aluminum is commonly used in high-energy systems: in thermite compositions, mixed fuels, and explosives, as well as in designs for the self-propagating high-temperature synthesis of refractory compounds. The reactivity of aluminum powders largely depends on the particle size and increases significantly when moving to particles smaller than 1 μm [25]. The use of finely ground aluminum powder in mixed fuels increases the specific thrust of engines, improves their start-up reliability, and increases the stability of fuel combustion [26,27].

Micron-sized aluminum particles only burn due to diffusion of the oxidizing agent through the oxide film on the surface of the particles. The burning rate depends on the diffusion rate. When aluminum melts inside a particle, the volumetric expansion and increased internal pressure result in the peeling of the oxide shell and splashing of molten aluminum, with oxidation in the gas phase [28–30]. The combustion scheme of an aluminum particle is shown in Figure 2. Figure 2 shows the combustion model of an aluminum particle. This model was developed to describe the combustion of aluminum in rocket engines. In rocket engines, the aluminum particle typically ignites near the surface of the propellant. Hence in this model, ignition is initially assumed to have occurred, and the model concentrates on the combustion after the ignition.

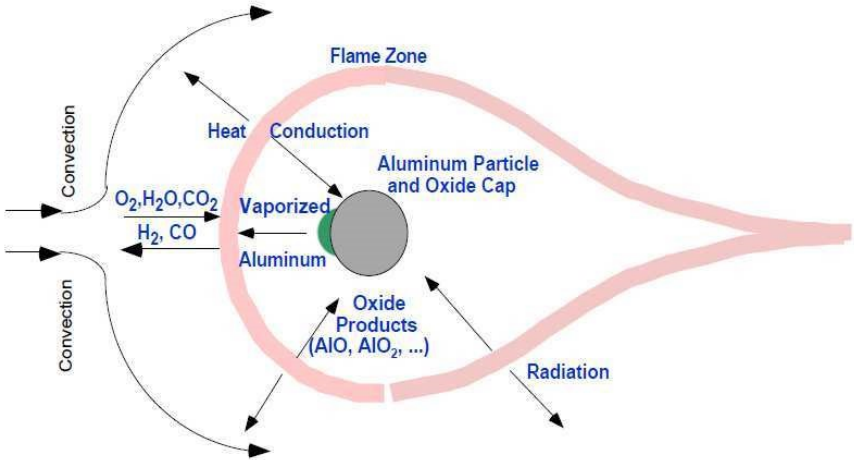


Figure 2. Combustion of an aluminum particle [30].

According to this combustion mechanism, we can assume the following: (1) The particle is spherical; (2) The flow around the particle is laminar. The flow around an aluminum particle under rocket engine conditions is usually laminar, due to the small particle size (typically less than 200 mm in diameter); (3) The local homogeneous flow model is applicable to liquid aluminum [30].

The traditional methods of activating aluminum and magnesium metals use the preparation of alloys. For aluminum, these are alloys based on mercury or gallium, with additions of indium, tin, thallium, and some other metals; for magnesium, alloys with nickel are used. The aluminum activation method uses the immersion of aluminum into gallama, in the range of melting temperatures of gallama and/or aluminum, in the presence of ultrasonic vibrations. Obtained using alkox technology, aluminum oxide differs in its structural and textural characteristics. The main disadvantages of this method are the following: first, the need to introduce metals in the form of chips. As is known from practice, the grinding stage is very laborious and is accompanied by an inevitable loss of metal. In addition, this method does not provide for the possibility of the regeneration of gallium, for its reuse [31].

To increase the activity of aluminum and other metals used as fuel in energy-intensive systems for various purposes, it is necessary, not only to increase the dispersion of powders,

but also to change the structural characteristics both in the volume and on the surface of the particles. The processing of metal powders in dynamic mills changes the surface energy and the internal energy of the residual stress zones in the ground particle presented as a "frozen" metastable state [32]. In this case, the change in the structure and form of the surface oxide layer of particles due to using various organic additives during the MCT of aluminum is of great importance [33,34].

The stage-by-stage transformation of the surface layer and the subgrain structure of aluminum particles during the MCT process is presented in the model (Figure 3), which reflects the concept of the modification process of metal particles [34]. During the MCT, the following stages occur: destruction of the oxide layer on the surface of aluminum particles; a change in the subgrain structure, as a result of accumulation and redistribution of defects in the bulk of the particle; and the formation of an encapsulating layer of modifying organic additives on the surface of the particles.

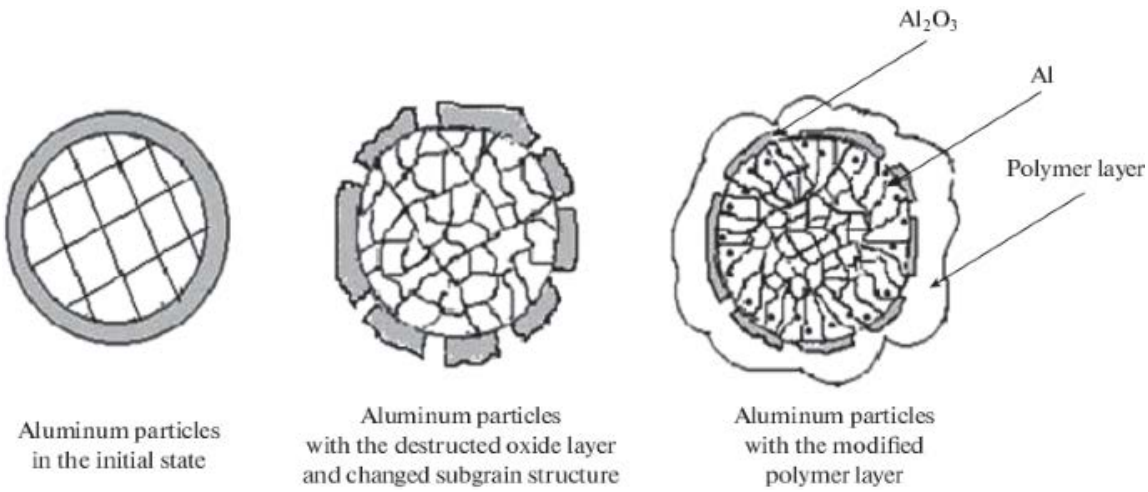


Figure 3. Model of the transformation of the surface layer and the subgrain structure of aluminum particles during MCT [34].

The destruction products of organic compounds during MCT, penetrating the near-surface layer along the subgrain boundaries, contribute to an increase in the activity of aluminum particles. Thus, a defective structure is formed and, consequently, the "excessive" energy of the system, ensuring its stable active state.

A change in the free energy of a substance under mechanical action is associated with distortions of the crystal lattice, an increase in its defectiveness, i.e., the formation of point defects in the crystal lattice or dislocations, or the destruction with the transition of a crystalline substance to an amorphous state. According to the dislocation theory, the activation of substances under mechanical action occurs due to dislocations emerging on the surface, due to the deformation of solids [35], leading to an increase in the chemical activity at the place where the dislocations occur. Numerous experiments have shown that the exit points of dislocations are indeed characterized by an increased chemical activity. High-frequency phonons accompany the motion of dislocations in a solid, due to the interaction of the developing dislocations with other dislocations, defects, impurity elements, or interfaces. In turn, high-frequency phonons can initiate chemical reactions.

As shown in [7], mechanochemical reactions are associated with the presence of short-lived active centers (SLCs). The death of the SLCs is the relaxation of excess energy. The end of SLCs is usually an exothermic process, accompanied by luminescence or other phenomena, due to the emission of energy observed during MCT. The degree of grinding and activation of metal powders, particularly aluminum, depends on the processing conditions (time, medium, and speed), the energy intensity of the mechanical reactor, and the choice of the additives that contribute to the grinding of metal particles. The use

of organic carbon substances has proven to be the most effective. Thus, due to processing aluminum with graphite, it is stated that aluminum is characterized by an anomalously high reactivity [36,37], which is associated with an increase in the specific surface area of particles and a change in the state of their crystal structure (changes in the size of the coherent scattering regions and relative lattice deformation). Mechanically, it is possible to obtain nanopowders with a particle size from 5–10 to 200 nm.

The presence of aluminum nanoparticles in fuel systems significantly changes the ignition and the entire combustion process [38,39]. The introduction of even a tiny amount of aluminum nanoparticles into hydrocarbon fuel systems intensifies the oxidation of hydrocarbons. This leads to the development of a chain mechanism in the combustion process. Using the example of a mixture of nano-aluminum with ethanol, the result of a chain combustion mechanism is shown [40], which ensures a high flame propagation rate, due to an increase in the diffusion rate of the active components of the chain process (Figure 4).

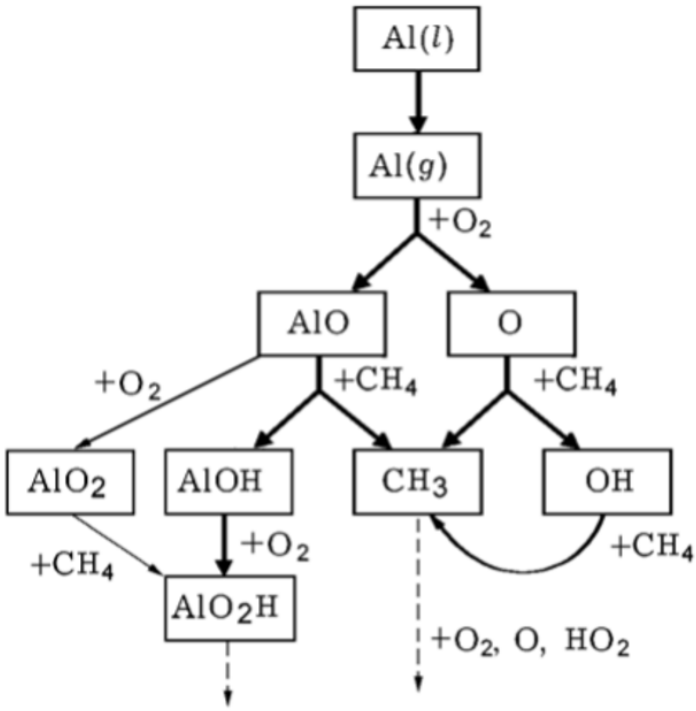


Figure 4. Hydrocarbon fuels containing aluminum particles will also have a higher flame propagation velocity. The acceleration is conditioned by an increase in the rate of diffusion of active radicals, from the hot to the cold zone of the flame.

As a result of such a chain reaction, and as shown in [40], hydrocarbon fuels containing aluminum particles will also have a higher flame propagation velocity. The acceleration is conditioned by an increase in the rate of diffusion of active radicals from the hot to the cold zone of the flame.

An increase in the activity of metal powders also occurs due to their mechanochemical treatment with various oxides, the presence of which ensures the minimum size of metal particles and their maximum defectiveness [41,42]. An increase in the activity of the obtained composite systems is then realized in the combustion processes, particularly in the SHS, increasing the combustion rate up to the detonation reaction mode.

An increase in the reactivity of aluminum particles due to mechanochemical treatment is of particular interest in the manufacturing of metalized solid propellants (SRPs). Most of the currently known solid rocket fuels contain up to 15–20% aluminum powder as a metal fuel, thus making it possible to significantly increase the combustion temperature, the product outflow rate, and, consequently, the efficiency of rocket fuel, providing an increase in flight range and the possibility of delivering a larger mass. Activation of aluminum

powders allows for an increase in the ballistic characteristics of propulsion systems in a wide range of values.

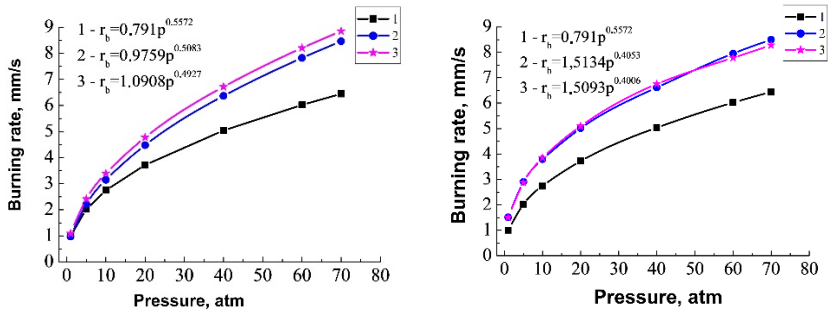
Modern mixed solid rocket fuels (SRT) usually consist of ammonium perchlorate, which acts as an oxidizing agent, aluminum in a finely dispersed spherical powder, and an organic polymer, as a binder. The metal and polymer play the role of fuel. Metal is the primary energy source, and the binder is the primary source of gaseous products. Due to the high boiling point, aluminum oxide cannot be in gas form in a rocket engine. It cannot do work when expanding in a nozzle. The combustion process of such systems largely depends on the dispersity, the shape of aluminum particles, and the density of the combustible mixture [43,44].

Studies of the effect of MCT on ballistic properties when using a mixture of PA/Al/HTPB (68%/18%/14%), and where the PA was ammonium perchlorate and HTPB was polybutadiene with terminal hydroxyl groups of grade R-45, which was used as a binder between the fuel and an oxidizing agent, showed a significant effect of the pretreatment of aluminum with modifying organic additives (in the presence of SiO_2) on the combustion rate of the SRF mixture [45].

$$r_b = aP^n \quad (1)$$

where r_b is SRF burning rate; a is the constant of proportionality; P is the pressure inside the combustion chamber; n is the pressure exponent.

The ballistic characteristics of solid propellants are presented in Figure 5a. The use of activated aluminum contributed to an overall increase in the burning rate of the SRF. It follows from the figure that the combustion rate of the composition with (Al + 20% $(C_2H_3OH)n$ + 20% SiO_2) increases by 25%, and the pressure exponent decreases from 0.5572 to 0.4927.



(**a**) (**b**)

Figure 5. Change in the burning rate for PA/HTPB/Alx fuels with non-activated aluminum (1), after MCT with a composite (**a**)—[Al+20%$(C_2H_3OH)n$ +5%SiO_2] (2) and [Al+20%$(C_2H_3OH)n$ +20%SiO_2] (3) and with composite (**b**)—Al+3% $C_{17}H_{35}COOH$ +5%SiO_2 (2) and Al+3%$C_{17}H_{35}COOH$ +20%SiO_2 (3) [45].

The best result in terms of burning rate and pressure exponent was demonstrated by compositions based on PA/HTPB/(Al+$C_{17}H_{35}COOH$+SiO_2) (Figure 5b). At present, stearic acid is used in the industrial scale passivation of aluminum powders. First, stearic acid is hydrophobic, second, during MCT, it fills cracks in the oxide film on the surface of aluminum particles, and third, it increases the chemical resistance of aluminum with respect to other fuel components, thereby increasing the shelf life of SRF. Aluminum particles in the composition of solid rocket propellants are initially localized between large oxidizer particles. Upon reaching the melting point of 660 °C, aluminum particles pass into a liquid state, but at the same time they are still within the volume of the oxide film, i.e., in an isolated state. The melting point of alumina is three times that of aluminum. In our case, liquid aluminum can flow out due to cracks in the oxide shell formed during the MCT and filled with stearic acid, which can facilitate ignition of the particles. The subsequent agglomeration of particles can occur in the heating zone adjacent to the burning surface layer.

After the introduction of a mechanically activated composite (Al + 3% C17H35COOH + 5% SiO_2) into the composition of the SRF, a good increase in the combustion rate was observed, from 13.5% at 5 atm to 15.9% at 40 atm. The use of powder (Al + 3%C17H35COOH + 20%SiO_2) caused only minor changes in the combustion rate compared to (Al + 3% C17H35COOH + 5% SiO_2), within Δrb = 17.6% in the considered pressure range. At the same time, the content of active aluminum, which was determined by the volumetric method, in the system was no more than ~85.1%. A possible factor in this result is that the active combustible system is a completely composite [Al + 3% C17H35COOH + 20% SiO_2] [45].

An advantage of using aluminum powders as an ingredient in solid fuels is the high heat generated during combustion. Due to this, the heat released during t oxidation of the metal increases the flame's temperature. For this reason, the value of the specific impulse in the aluminized fuel is increased by 10%. In addition, there is another important characteristic: the unstable combustion of aluminum and systems based on it, which is essential when using aluminum in condensed systems. An analysis of the effect of additives of powdered aluminum, including nanosized particles, on the propelling ability of explosive compositions is described in [46]. The addition of highly dispersed aluminum can increase the propelling power of pieces of pure combustible substances (ES). The addition of nanosized aluminum also makes it possible to increase the propelling ability of explosives. However, the observed increase is somewhat lower than micron-sized aluminum, due to the high content of oxide on the surface of the nanoparticles.

On the other hand, the addition of aluminum powders to the composition of rocket fuel also has a negative impact: a two-phase flow, which provides additional losses in specific impulse, luminescent (luminous) exhaust trails, slag accumulation, nozzle erosion, and a high temperature of the combustion products. Since most of these problems are associated with the formation of condensed combustion products, many investigations have focused on the need to understand the mechanisms of combustion and the accumulation of aluminum particles. Many works have aimed to find a solid fuel that produces as few condensed combustion products as possible, with a minor proportion of unburned aluminum. According to the results of the studies in [47], concentrated combustion products (CCPs) can be divided into two types: agglomerates, and fine oxide particles (FOPs). The agglomerates are typically 100 μm or more significant in size and are formed by the adhesion of aluminum particles. Agglomerates may contain alumina and other condensed products, and they can reduce fluctuations up to 500 Hz. The particle size of FOPs is about 1 μm, and they are formed as a result of the combustion of one particle, as well as due to the explosion of the non-agglomerated fraction of the metal; the frequency they can lower to is about 4000 Hz.

These agglomerates interfere with the uniformity of fuel combustion, leading to a decrease in gas generation, a reduction in the fuel burning rate and the amount of heat released during the reaction, and a decrease in the specific impulse of the rocket. When the metal concentration in the fuel exceeds the set threshold, the agglomeration process becomes dominant and increases with the increase in the metal particle size in the fuel mixture.

The increase in volumetric and gravimetric specific impulses, which determine the spacecraft's performance, is significant for the actual volume of the propulsion system and the amount of fuel needed for a particular mission. Solid propellants must meet specific compactness requirements and have a high density, but have limited gravimetric specific impulse values compared to other fuel systems (hybrid and liquid) [48,49].

3. Prospects for the Use of Mechanochemical Processing for the Production of Physiologically Active Drugs from Plant Materials

One of the most effective areas of the application of mechanochemical processing has been the processing of plant materials. Impressive results have already been achieved in this direction. The central concept of mechano-chemical technologies is that carrying out reactions in the solid phase shortens the technological chain [50]. Plant material is

a composite material: it is complex structured and contains many different components. Cells of higher vascular plants (for example, cereals) can be non-lignified and lignified. In the first case, cell membranes contain only structural carbohydrates (cellulose and hemicellulose), so they are easily crushed during mechanical processing. Lignified cells also have lignins, which are complex, chemically stable polymer formations that give the cell membrane strength.

Using the mechanochemical processing of various plants, products for pharmaceuticals, animal husbandry, veterinary medicine, plant growing, etc., can be obtained [4,51]. The efficiency of mechanochemical processing of plant raw materials can be increased by carrying out a preliminary chemical or biochemical treatment, in such a way as to break the bonds between the main macrostructural elements; for example, between lignin and hemicellulose. With the help of the mechanochemical approach, many useful preparations were obtained at the ICTTM SB RAS. For example, environmentally friendly substitutes for feed antibiotics. Substitutes for antibiotics are mannan-oligosaccharide preparations obtained from the cell walls of microorganisms (yeast and fungi). Preparations containing triterpene acids are obtained from coniferous trees, which can be used instead of very expensive plant growth regulators [52]. Millet husk contains a large number of phytosterols. However, it is not possible to use the husk as a feed additive; phytosterols are not absorbed in the animal's digestive tract. In a mechanochemical product, they change into a soluble complex. However, the main mechanochemical "topic" in bio-additives is the development of technology for antioxidant preparations containing soluble chelated forms of silicon. This drug is obtained from rice husks, and the silicon dioxide located there is converted into a soluble form with the help of green tea gallocatechin [53,54].

In recent decades, special attention has been paid to the mechanochemical processing of material from plant materials, with their subsequent use in the production of medicines, i.e., in pharmaceutical technology [4,55]. Thus, the effect of the mechanochemical processing of potato and corn starches on their physicochemical and technological characteristics in pharmaceutical preparations was considered [56]. Starch is used as a binding, loosening, and antifriction agent, as well as to provide the necessary technological properties for granules and tablets, and also reduces the concentration of starches in prolonged dosage forms, while maintaining the high viscosity of the dispersion medium.

Mechanochemical treatment of medicinal substances (MS) in the presence of various auxiliary additives (for example, acetylsalicylic acid with plant flavonoids) contributes to an increase in solubility; i.e., their effectiveness [57]. This is due to a decrease in particle size, modification of the crystal structure, and the formation of solid dispersions in which medicinal substances are dispersed in molecular form or in an amorphous state, with the construction of water-soluble complexes, etc. (Figure 6).

Mechanochemical treatment of substances leads to an increase in the area of grain boundaries and the formation of new surfaces [58]. A technique has been developed for the mechanochemical preparation of supramicrostructured forms for the prolongation of different chemical natures (Na-CMC—sodium carboxymethylcellulose, PVA—polyvinyl alcohol, a combined prolongation of Na-CMC and PVA in various ratios), and it has been shown that, as a result of such processing, a change in the shape and size of the particles occurs, as well as the accumulation of microparticles [59]. As a result of the solid-phase mechanochemical treatment of prolongation, the rheological parameters of aqueous solutions change; in particular, the viscosity increases. With an increase in the duration of the mechanochemical treatment of the prolongation of different chemical natures, an increase in the kinematic viscosity of the aqueous solutions is noted. The use of an effect discovered for increasing the density in the development of formulations and the technology of prolonged liquid dosage forms, in particular ophthalmological ones, will make it possible to reduce the concentration of the prolongation, while maintaining the high viscosity of the dispersion medium. Presumably, eventually, the use of such prolongation in the composition of drugs will contribute to their bioavailability and therapeutic efficacy.

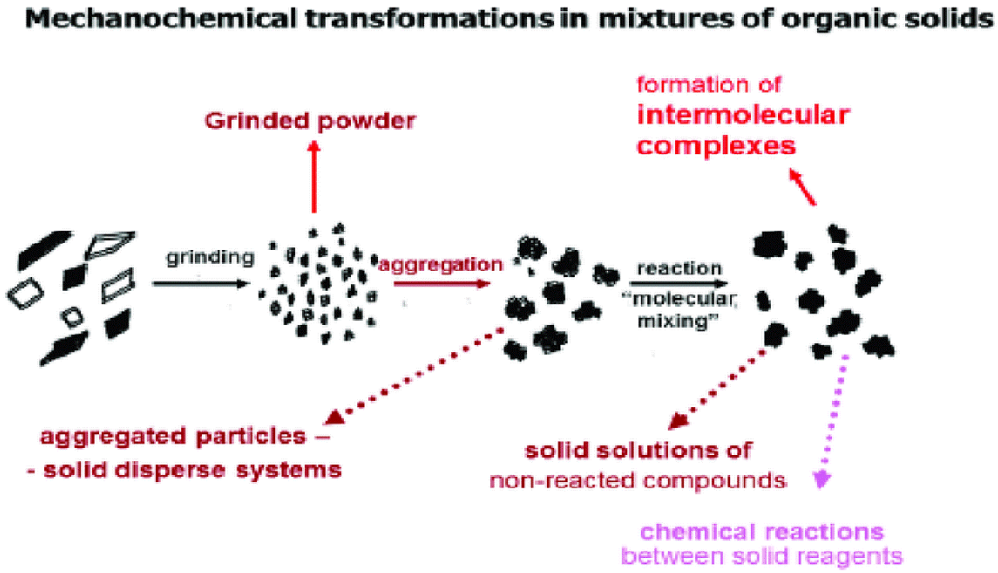


Figure 6. Scheme of mechanochemical transformations in mixtures of solids (drugs + excipients) during mechanochemical processing [57].

Mechanochemical treatment isolates biologically active substances from plant materials, particularly water-soluble salt forms of triterpene acids and dichloroisocyanuric acid [60]. The practical significance of the studies carried out lies in using these drugs as regulators of the growth and development of plants and animals in agriculture. Using the example of triterpene acids, phytoecdysteroids, and phytosterols, it has been shown that the solubilization of sparingly soluble organic compounds can be based on known physicochemical effects that can be carried out mechanochemically in situ, i.e., in the matrix of raw materials that are usually used for extraction.

In [61], a comparative analysis of various methods for the extraction of plant raw materials is given. Figure 7 shows a scheme of the most common extractions and uses of mechanochemical processing.

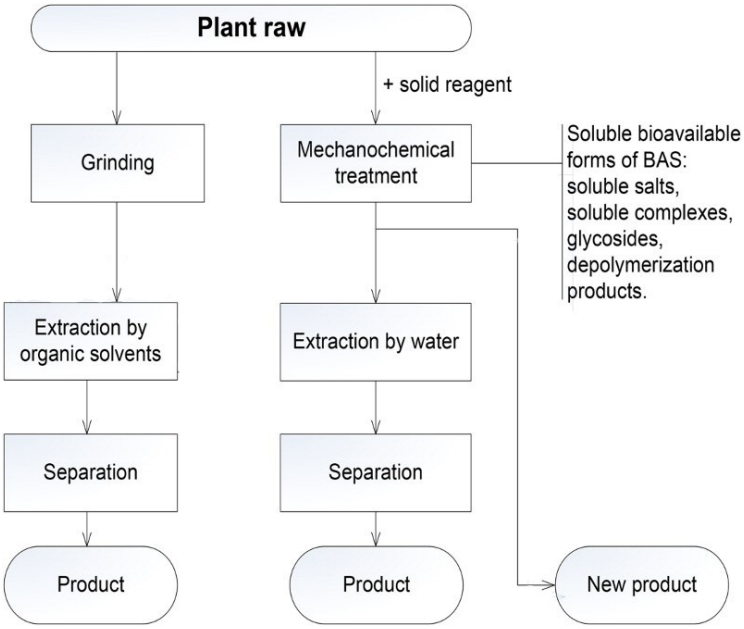


Figure 7. Comparison of the best-known methods for the separation of biologically active substances and mechanochemical extraction from plant materials [61].

According to the generally accepted extraction scheme, vegetable raw materials are crushed and extracted in various organic solvents with different polarities. The final stage of these technologies is separating the extract by evaporation of the solvent. During mechanochemical extraction, a mixture of plant materials and a solid reagent is processed in mechanochemical reactors; as a result of this processing, the target substance is converted into a chemical form with the highest solubility in water. The extract, in this case, is isolated with water. The product can be obtained in a higher yield and higher purity than extracts isolated using organic solvents. The product obtained by mechanochemical treatment has the same properties as the products of traditional extraction technologies. The undoubted advantage of the mechanochemical method is the reduction in the number of stages required to give the product the desired properties and the ease of organizing production.

Production of phenolic compounds of plant origin during the mechanochemical processing of a structured multicomponent system using vegetable raw materials (green tea *Camellia Sinensis* L., St. Jon's wort *Hypericum perforatum* L.) for preparations of phenol compounds, catechins and gallocatechin of tea and dianthrone compounds of St. Jon's wort in a soluble biologically accessible form, was considered in [62]. Changes in the structure of the vegetable raw materials at the macro and micro levels during mechanical processing under various conditions were studied. The threshold nature of the dependence of the degradation rate of antioxidant compounds in plant raw materials on the intensity and the time of mechanical treatment was found; and the conditions for processing green tea and St. John's wort were determined, as a result of which a powdered product was formed without degradation of the target compounds. Based on these studies, methods for obtaining powdered products were developed [63]. The catechin-containing products were characterized by a 40% increased water-soluble green tea catechins yield and a twofold increase in shelf life. The hypericin-containing products were characterized by a 12-fold increase in the content of soluble hypericin. These products can be used as a food additive in medicine and animal husbandry, as preparations with an antioxidant effect.

The use of the mechanochemical processing of plant materials together with various reagents makes it possible to obtain reactive mechanocomposites. As shown in [64,65], chemical reactions involving such mechanocomposites proceed more efficiently, due to a decrease in diffusion paths and an increase in the stability of the target substances or enzymes (in the case of enzymatic processes), as a result of mechanochemical processing, the reactivity of the substances that make up the plant material increases due to the increase in the specific surface area, a decrease in the crystallinity of cellulose, and a general disordering of the supramolecular structure of the cell walls.

The efficiency of mechanochemical processing of plant raw materials largely depends on the choice of process parameters that ensure the destruction of cells and the isolation of the necessary compounds. These parameters include material, size and density of grinding balls, chamber filling and mixing speed, grinding time, suspension composition, etc. (Figure 8).

The optimal selection of parameters provides the advantage of a mechanochemical process with a high degree of destruction of various plants and microalgae, increases the yield of bioactive products during extraction, and allows solubilization of substances in water at room temperature instead of using organic solvents, reducing the extraction time and simplifying the purification steps [66].

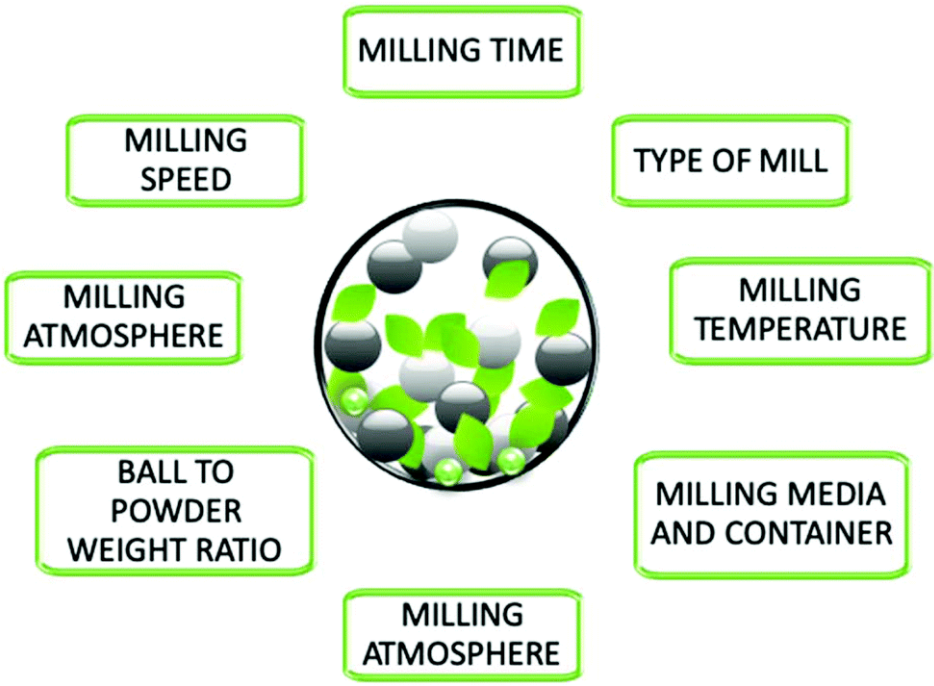


Figure 8. Parameters of the mechanochemical processing of vegetable raw materials [66].

Much attention has been paid to the mechanochemical processing of wood, which is a raw material for producing various products. The most modern and most promising technological process is the mechanochemical modification of wood. This technology consists of the impregnation of the wood substance with an aqueous solution as a modifier, which enters into a chemical reaction with the natural components of the tree during thermal and mechanical activation. The modifier, in the proposed technology, is carbamide; a substance that not only can react with the elementary components of wood, but also dramatically enhances the effect of the functional additives added to the modifier, to give the wood product the specified physical, mechanical, and operational properties. The modifier, penetrating with the help of water to the cellular level of the wood substance and reacting with it, changes the structure of the wood in the manner desired by the manufacturer of products from mechanochemically modified wood (MCMW). An MCMW product may be hydrophobic or non-combustible. It is possible to change the color and texture of the original wood, the density and strength of MCMW, as well as the hardness, abrasion, and technological properties.

The combination of the developed technologies for mechanochemical modification of wood makes it possible to create a multidisciplinary production unit and easily switch from the production of non-pressed moldings, for example, to the production of parquet boards from solid wood, facing products or doors, furniture elements or finishes, according to orders, which dramatically expands the scope and opportunities of the sales market. Some of these technologies are exclusive. Mechanochemically modified wood is at the stage of being introduced to the market, and the technology is at the stage of implementation and optimization; that is, from both an economic and technical point of view, we are talking about innovative technologies that allow creating a new material with the desired properties.

Mechanochemical processing is also used in the pulp and paper industry to prepare cellulose-containing fibers in the presence of, for example, alkali to reduce the content of extractive substances in cellulose: resins, and fats. Under mechanical action, the destruction of cellulose occurs, namely, the rupture of glycosidic and carbon-carbon bonds, i.e., a decrease in the degree of polymerization of cellulose and a change in the reactivity of cellulose under the action of mechanical forces. The possibility of breaking chemical bonds

in macromolecular compounds under mechanical impacts (grinding, crushing), leading to the destruction of macromolecules, was reported for various classes of polymers; in particular, starch and cellulose methylcellulose polystyrene. Systematized data on the processes of mechanochemical degradation of polymers are given in the monograph by Baramboim. For cellulose and its derivatives, it has been reported that, under the action of a mechanical force, both the initiation of the actual destruction (breaking of the central valence bonds) and the activated mechanochemical destruction associated with hydrolysis alcoholysis, aminolysis, etc. are possible.

Technological processes for alkaline extraction and pulp bleaching with hydrogen peroxide were developed on specially designed apparatus for the mechanical processing of high-concentration pulp [67]. It has been stated that in the process of mechanochemical treatment, degumming takes place and an increase in the reactivity of cellulose to viscose formation [68]. The development of technical solutions that significantly reduce the mass fraction of resins and fats in unbleached viscose cellulose before bleaching will ensure a high quality of viscose pulp, in terms of resins and lard and, at the same time, increase the product yield, and save chemicals and energy. The stated changes in cellulose structure as a result of mechanochemical processing are a new stage in the evolution of the technology in the pulp and paper industry. The high value of the reactivity index after MCT does not allow the possibility of using cellulose for paper in the production of chemical fibers. Nevertheless, this only indicates a significant effect of reagents on cellulose macromolecules in cell walls. Both the technical cellulose and waste fibers of medium and high concentration are subjected to mechanochemical processing.

4. Conclusions

1. An analysis was made of examples of mechanochemical treatment (MCT) of various materials, of both mineral and vegetable origin, and both metal and polymer systems, as well as the use of various methods of mechanical action in the systems under study (treatment in activator mills or ultrasonic treatment), demonstrating the significant possibilities of MCT for obtaining materials for a wide range of purposes.

2. The effect of mechanochemical treatment and the nature of the modifier on the microstructure and reactivity of activated and modified aluminum was studied. A change in the state and composition of the surface oxide layer of aluminum particles after MCT, its saturation with an organic modifier, and the stabilization of structural changes were shown. The high activity of metal particles in Al/modifier and Al/modifier/SiO_2 composites is due to the transformation of the structure of the surface layer and the minimum size of crystallites (i.e., high defectiveness of particles), which together determine a high level of reactivity when they are used as part of combustible condensed systems.

3. The optimal conditions for carrying out the MCT process of aluminum with various modifiers (stearic acid, polyvinyl alcohol), and which ensure the formation of an organic surface layer protective against oxidation during storage in air and the activation of chemical reactions in combustion processes, were determined. A maximum increase in activity after MCT of aluminum by 20 and 25% was established as a result of the MCT of the Al/modifier/SiO_2 composite with 20% polyvinyl alcohol and 3% stearic acid, respectively, at a SiO_2 content of 20 and 5%. Silicon dioxide in an aluminum-based composite plays the role of a promoter of the combustion of condensed systems.

4. The prospects for the use of MCT for the production of physiologically active preparations from plant materials were presented, which is an effective way to create new materials in the field of pharmaceuticals, animal husbandry, veterinary medicine, plant growth, etc. After MCT, substances can be obtained with a higher yield and higher purity, compared with extracts isolated using organic solvents. The advantage of this method is the reduction in the number of stages and equipment required to give the product the desired properties, as well as the ease of production.

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methodology, software. A.B. (Aisulu Batkal): Conceptualization, methodology, software. A.K.: Visualization, Investigation. N.M.: Writing-reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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