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ИСПОЛЬЗОВАНИЕ МЕХАНОХИМИЧЕСКОЙ АКТИВАЦИИ ДЛЯ РЕГУЛИРОВАНИЯ РЕОЛОГИЧЕСКИХ СВОЙСТВ ФОРМОВОЧНЫХ МАСС ДЛЯ ЭКСТРУЗИИ КАТАЛИЗАТОРОВ И СОРБЕНТОВ

Было исследовано влияние влажности, измельчения и механохимической активации твердой фазы на реологические свойства формовочных паст для экструзии катализаторов и сорбентов. Были проанализированы такие параметры формовочных паст, как прочность коагуляционной структуры, индекс течения, наибольшая пластическая вязкость, предельное напряжение сдвига, пластичность, период релаксации, соотношение деформаций. Для характеристики степени механохимической активации были использованы размер области когерентного рассеяния и величина микродеформаций. Было показано, что увеличение степени механохимической активации твердой фазы позволяет регулировать свойства формовочных паст в более широком диапазоне. В технологии экструдированных катализаторов и сорбентов предложено использовать мельницы-активаторы с ударно-сдвиговым характером нагружения. Были рекомендованы мельницы со средним значением энергонапряженности (до 6 кВт/кг).

Ключевые слова: механохимическая активация, реология, экструзия

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USE OF MECHANOCHEMICAL ACTIVATION TO CONTROL RHEOLOGICAL PROPERTIES OF MOULDING PASTES FOR CATALYSTS AND SORBENTS EXTRUSION

The influence humidity, grinding and mechanical activation of the solid phase on the rheological properties of the molding paste for extrusion of catalysts and sorbents was studied. The following parameters of the molding pastes were investigated, namely the coagulation structure strength, the flow index, the maximum plastic viscosity, the critical shear stress, plasticity, the r (stuelaxation period), the ratio of deformations. In order to characterize the degree of mechanochemical activation, the dimension of the coherent scattering region and the microdeformations value were used. Increasing the degree of mechanochemical activation of the solid phase was shown to allow controlling the properties of molding pastes in a more wide range. In the technology of extruded catalysts and sorbents, the mills-activators with the impact-shear loading are proposed to use. The mills with an average value of power density (up to 6 kW/kg) were recommended.

Key words: mechanochemical activation, rheology, extrusion

Mechanochemistry has received quite a rapid development in recent years. The basic amount of research is aimed at obtaining the new materials [1, 2]. However, mechanochemistry is also a powerful tool with which it is possible to control the properties of the systems on the subsequent grinding stage. In particular, activation of the solid phase enables significantly affect rheological properties of pastes for extrusion of bulk products from the powders [3].

The obtained by extrusion molding the products occupy a significant place in the nomenclature of manufactured catalysts and sorbents [4]. For the success of the extrusion molding, the rigid requirements are imposed on rheological properties of molding pastes [5, 6]. To control the properties of molding pastes, it can be employed such methods as dispersion change of solid, humidity change, as well as the change of physicochemical properties of the surface, the introduction of electrolyte additives, surfactants and materials with other structural and mechanical properties of [5, 7]. Methods for measuring the rheological properties of disperse systems were developed [5, 7-12]. Tests on the rheometers with parallel-shifting plates (maximum plastic viscosity η_1, critical shear stress P_{k1}, plasticity Ps, relaxation period Θ, the deformation relationship, etc.) [5, 7-11], as well as the rotational and capillary viscometry (power to the destruction of the coagulation structure ΔN, the flow index n and others) [5-12] have become widespread. The detailed description of the equipment and methods of investigation are given in Refs [5, 9].

Thus, the comparison of mechanochemical activation (MCA) with traditional methods of controlling the properties of molding pastes is of interest.

The simplest way to control the rheological properties of the pastes is a change in humidity. Thus, the increase in the content of the liquid phase in the dispersion increases the proportion of plastic deformation ε_{pl} (Fig. 1), plasticity increase Ps and reducing the critical shear stress P_{k1} (Fig. 2). But the possibilities of this method are limited. It was demonstrated that there is a relatively narrow range corresponding to optimal humidity with fixing solids particles in the near potential minimum [5]. This is such a state of a disperse system in which all particles are covered a layer of a solvate and the free liquid is absent. In Figure 2 for this state, the humidity range 25-27 wt.% is responsible, where there is an inflection at the dependences P_{k1} vs Ps. The disadvantage of the liquid phase results in brittle failure of molded pellets, but excess leads to excessive flowability that causes severe deformation of the extrudate under its own weight.

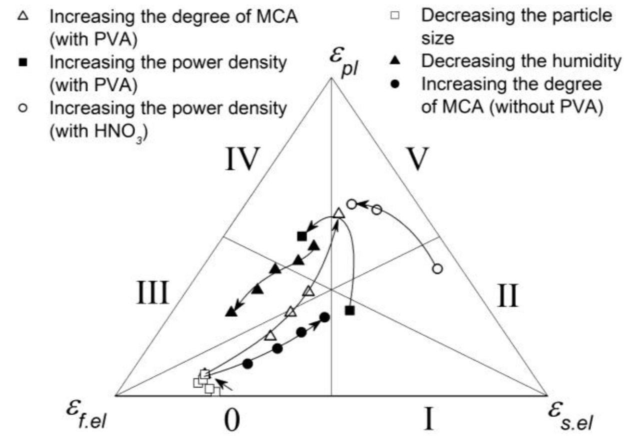


Fig. 1. Diagram of development of the deformations in the molding pastes [3, 21, 22] ($\varepsilon_{f.el}$, $\varepsilon_{s.el}$, ε_{pl} are 100% fast elastic, slow elastic and plastic deformations, respectively; Roman numerals are the number of structural and mechanical type). Ingredients of molding pastes: solid phase is alumina (60 wt.% α-Al_2O_3 and 40 wt.% γ-Al_2O_3), the liquid phase is the 5 wt.% aqueous solution of polyvinyl alcohol (PVA), or the 20 wt.% solution of nitric acid

Рис. 1. Диаграмма развития деформаций в формовочных пастах [3, 21, 22] ($\varepsilon_{f.el}$, $\varepsilon_{s.el}$, ε_{pl} – 100% быстрых эластических, медленных эластических и пластических деформаций, соответственно; римские цифры – номер структурно-механического типа). Компоненты формовочных паст: твердая фаза – глинозем (60 мас.% α-Al_2O_3 и 40 мас.% γ-Al_2O_3), жидкая фаза – 5 % водный раствор поливинилового спирта (ПВС) или 20 % раствор азотной кислоты

Initial raw material for the preparation of catalysts and sorbents is the polydisperse powders. Negligible fine fraction content determines the low ductility [13-16], and as a result, the pastes have poor moldability. For dispersing a powders, the various designs of the grinding devices are used, which are classified according to the transfer method of a mechanical impulse from the grinding body to the material [1, 2, 17]. The shape of grinded particles depends on the method of mechanical energy loading. When using mills with impact-shear loading (balls, vibratory, planetary, and the like) the particles have a shape close to the bowl. In mills with impact loading, the particles have an irregular shape with sharp corners and cleavages. In Refs. [5, 16], it was shown that the particles must have to have a spherical shape to produce pastes which are suitable for extrusion, i.e. it is preferred to use the impact-shear milling device. When the molding paste is prepared from the powder with the spherical particles, its rheological properties are isotropic and the unpredictable character does not occur in the extrusion flow [6].

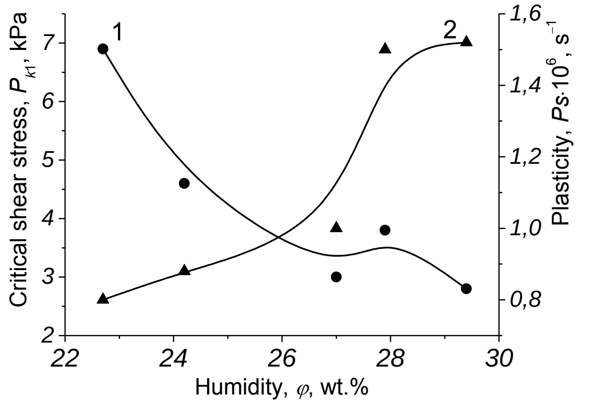


Fig. 2. Dependences of the critical shear stress and the plasticity of pastes based on ZnO on humidity [23]. Ingredients of molding pastes: solid phase is zinc oxide; the liquid phase is the 5 wt% aqueous solution of polyvinyl alcohol (PVA). 1 – P_{k1}, 2 – Ps

Рис. 2. Зависимости предельного напряжения сдвига и пластичности паст на основе ZnO от влажности [23]. Компоненты формовочных паст: твердая фаза – оксид цинка, жидкая фаза – 5 % водный раствор поливинилового спирта (ПВС). 1 – P_{k1}, 2 – Ps

Mills are differed both by method of a mechanical impulse loading, and by its power, which is characterized by the value of energy intensity (amount of energy which is loaded into unit mass of the material per unit time) [18]. If the mills have high energy intensity, apart from the actual grinding, the mechanochemical activation (MCA) processes of solid phase occur [1, 2, 17]. The stress fields which arise in the particle may relax on multiple channels, including chemical reactions [1, 2, 19]. During the preparation of molding pastes, a higher chemical activity of the solid phase in contact with the dispersion medium makes possible to obtain a more amount of bonds thereby significantly change the rheological properties of pastes [1, 2, 5].

A demonstration example of the influence change of the particle size of solid phase is the grinding of alumina in a laboratory ball mill. The effect of MCA in this mill is insignificant [20], so that all phenomena in the rheological behavior of molding pastes can be attributed only with a decrease in particle size. So, at the initial stage of grinding a substantial decrease of alumina particle size is observed (Fig. 3). In this case, the molding pastes show a sharp decrease in the critical shear stress P_{k1} and growth of the maximum plastic viscosity η_1. However, the deformation relationship changes little (Fig. 1). A further grinding in the ball mill leads to increased aggregation rate, resulting in dynamic equilibrium is established, and particle size substantially does not change. The rheological properties of the pastes are also not significantly changed (Fig. 3). Thus the particle size reduction during dispersion in the mills does not enable to vary the properties of molding pastes in a wide range.

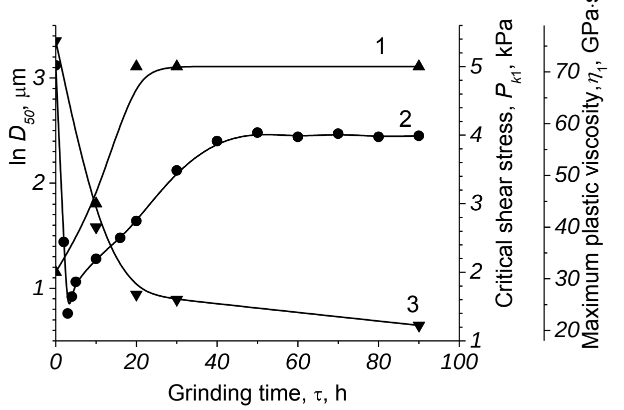
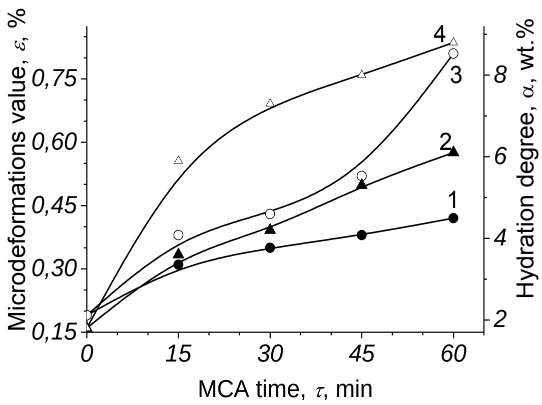


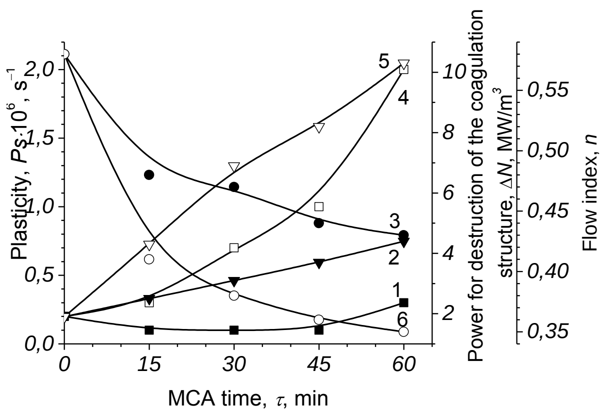
Fig. 3. Dependences of the average size of the alumina particles, the critical shear stress and maximum plastic viscosity for the pastes on its basis on the grinding time in the laboratory ball mill [21, 22]. Ingredients of molding pastes: solid phase is alumina (60 wt.% α-Al_2O_3 and 40 wt.% γ-Al_2O_3), the liquid phase is the 5 wt.% aqueous solution of polyvinyl alcohol (PVA). 1 – P_{k1}, 2 – $\ln D_{50}$, 3 – η_1

Рис. 3. Зависимости среднего размера частиц глинозема, а также предельного напряжения сдвига и максимальной пластической вязкости паст на его основе от времени измельчения в лабораторной шаровой мельнице [21, 22]. Компоненты формовочных паст: твердая фаза – глинозем (60 мас.% α-Al_2O_3 и 40 мас.% γ-Al_2O_3). Жидкая фаза – 5% водный раствор поливинилового спирта 1 – P_{k1}, 2 – $\ln D_{50}$, 3 – η_1

The use of energy-intensive mills allows to transfer the grinding process of the raw material to another qualitative level, namely, mechanochemical activation [1, 2, 17, 20]. So, the Al_2O_3 hydration degree increases after treatment into vibratory roller-ring mill during MCA (Fig. 4, *a*). In Refs. [5, 20], it was shown that the solid particles size and the coordination number are changed only during 10-15 minutes of grinding, and then remains constant. This means that increasing the amount of hydrated aluminum oxide cannot be explained only by increasing the specific surface area. Te reactivity growth was caused by an increase in defects in the crystallites. Greater amount of aluminum hydroxide on the surface of the particles allows the formation a sufficiently strong and deformable coagulation bonds. This has a positive influence on the rheological properties of the pastes. An increase in MCA time of alumina allows to significantly increasing the proportion of plastic deformation ε_{pl} to yield optimum ratio (Fig. 1). This is accompanied by the increase of plasticity *Ps*, the increase strength of coagulation structure of disperse systems Δ*N* and the reduction of the flow index values *n* (Fig. 4b). Note that all rheological parameters after MCA increases in several times, and these changes are correlated with the degree of alumina hydration.



a

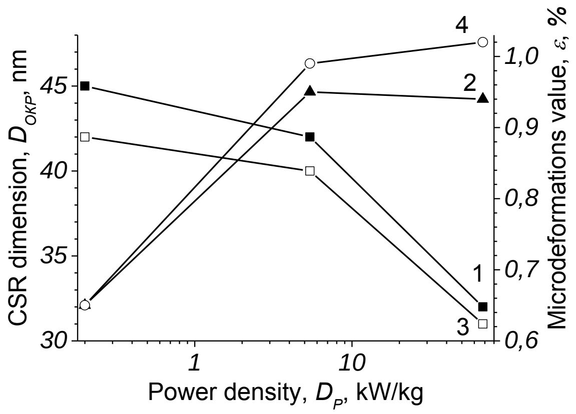


b

Fig. 4. Dependences of the parameters of mechanically activated alumina (a) (1, 3 – ε, 2,4 – α, 1, 2 – addition PVA, 3, 4 – addition-free PVA) and the rheological properties paste on its basis (b) (1, 4 – Ps, 2, 5 – ΔN, 3, 6 – n, 1-3 – addition PVA, 4-6 – addition-free PVA) on the time of mechanochemical activation [3]. Ingredients of molding pastes: solid phase is alumina (60 wt.% α-Al_2O_3 and 40 wt.% γ-Al_2O_3), the liquid phase is the 20 wt.% solution of nitric acid

Рис. 4. Зависимости параметров механически активированного глинозема (a) (1, 3 – ε, 2,4 – α, 1, 2 – addition PVA, 3, 4 – addition-free PVA) и реологических свойств на его основе (b) (1, 4 – Ps, 2, 5 – ΔN, 3, 6 – n, 1-3 – addition PVA, 4-6 – addition-free PVA) от времени механохимической активации [3]. Компоненты формовочных паст: твердая фаза – глинозем (60 мас.% α-Al_2O_3 и 40 мас.% γ-Al_2O_3), жидкая фаза – 20 % раствор азотной кислоты

As was mentioned above, the mill-activators are differed in the power density magnitude which determines largely the MCA effect [1, 2]. In Ref [20] it was shown that there is an optimal MCA time which is proportional to the supplied energy. Exceeding this time does not lead to a significant change in the MCA degree into the given mill, and the MCA effect is determined by the power of the supplied mechanical pulse in the mill. The increase in power density of a mill (ball < vibratory < planetary) gives a gradual decrease in the dimension of the coherent scattering region (CSR) (Fig. 5, *a*), while the size of the secondary aggregates does not change [20].



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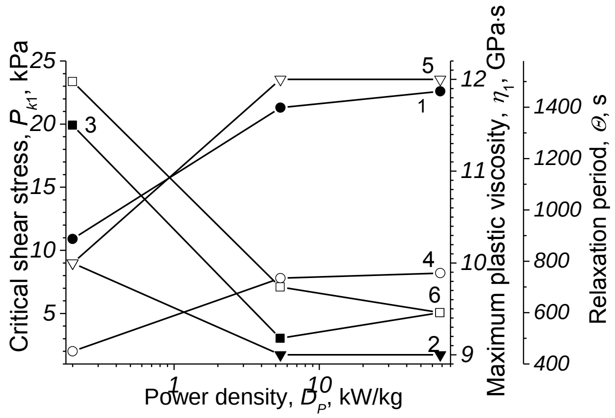

b

Fig. 5. Dependences of parameters of fine crystal structure of alumina (a) (1, 3 – D_{CSR}, 2, 4 – ε, 1, 2 – addition of PVA, 3, 4 – addition of paraffin) and the rheological properties of the paste on its basis (b) 1, 4 – P_{k1}, 2, 5 – η_1, 3, 6 – Θ, 1-3 – addition PVA, 4-6 – addition Paraffin) on the power density of mills with the impact-shear loading [3, 21, 23]. Ingredients of molding pastes: solid phase is alumina (60 wt.% α-Al_2O_3 and 40 wt.% γ-Al_2O_3) and 5wt.% paraffin, the liquid phase is the 20 wt.% solution of nitric acid

Рис. 5. Зависимости параметров тонкой кристаллической структуры глинозема (a) (1, 3 – D_{CSR}, 2, 4 – ε, 1, 2 – добавка поливинилового спирта, , 3, 4 – добавка парафина) и реологических свойств на его основе (b) 1, 4 – P_{k1}, 2, 5 – η_1, 3, 6 – Θ, 1-3 – добавка поливинилового спирта, 4-6 – добавка парафина) от энергонапряженности мельниц с ударно-сдвиговым характером нагружения [3, 21, 23]. Компоненты формовочных паст: твердая фаза – глинозем (60 мас.% α-Al_2O_3 и 40 мас.% γ-Al_2O_3) и 5 мас.% парафина, жидкая фаза – 20 % раствор азотной кислоты

Significant growth in the microdeformations value is observed only up to the power density value of the mill of the order of 4-6 kW/kg. Character changes defectiveness of alumina particles is correlated with a change in the rheological properties of molding pastes based on it. Maximal changes in the ratio of deformation (Fig. 1), P_{k1}, η_1 and Θ (Fig. 5b) are observed using the mill with power density of about 6 kW/kg. Should be noted that all the changes in the rheological behavior of the pastes have a positive effect on their moldability. Moreover, using activators with different power of the applied mechanical pulse, it is possible to vary the rheological properties within a wide range. Thus, changes in the rheological properties is directly related with MCA effect of the solid phase in the mills-activators, which allows to increase the amount of binder, that is produced in the process of preparing paste with stirring powder in a liquid phase, [3, 5].

It should be noted that the MCA degree which is required for the effective control by properties of the pastes can be obtained in the industrial mills [1, 2].

Fig. 6 shows how the pastes humidity decrease, particle size decrease and increase of MCA degree of solids influence rheological properties of the molding pastes.

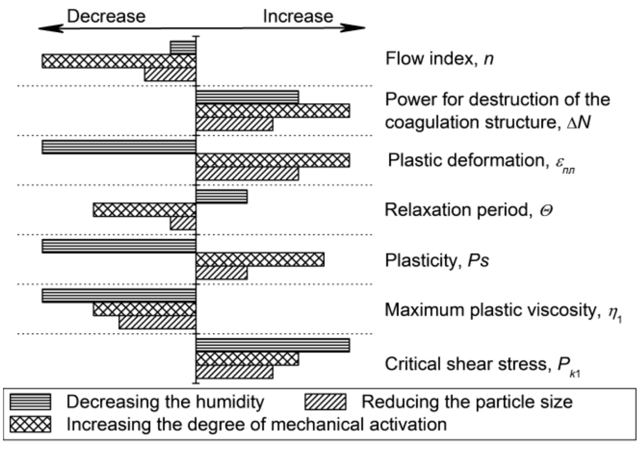

Fig. 6. Diagram showing the relative degree of influence of control modes on the rheological properties of molding pastes

Рис. 6. Диаграмма, показывающая относительную степень влияния способов управления на реологические свойства формовочных паст

CONCLUSIONS

The increase in the dispersion and the MCA degree of solids particles result in analogous qualitative changes in the rheological properties. Mechanochemical activation in the mills allows expanding the range of variation the pastes properties as compared with the grinding. Maximum control effect by the molding properties is achieved when use of mills-activators with an average value of the power density 3-7 kW/kg. A further increase in power density of mills does not give the substantial changes in the rheological behavior of the molding pastes. For carrying MCA of the solid phase, the mills with impact-shear loading are recommended to use.

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