Research of the possibility of producing finely divided materials from natural raw materials for reactive powder concretes by mechanochemistry

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Abstract. The results of mechanochemical activation of natural silica are presented in this paper. It is shown that disintegration activation allows the preparation of highly dispersed oxide powders.

Keywords. Mechanochemical modification, disintegrator, silica, oxide materials

Introduction

In modern industry, the direction of obtaining highly dispersed materials continues to develop rapidly. They are widely used in construction, in the production of fire extinguishing powders, in the petrochemical, paint and varnish and rubber industries. Usually, we talk about the amorphous form of silica (white soot and aerossil) or aluminosilicates, which play the role of a carrier on the surface of which water repellent is grafted.

Reactive powder concretes are multicomponent materials, which include both highly dispersed and modified oxide powders [5, 6]. In industry, for example, quartz flour obtained by grinding with an average particle size of 17 and 34 microns is used as such fillers [12].

Grinding materials is an energy-intensive process. The issue of specific grinding energy is global, since it takes 3-4% of all energy generated on the planet to grind. The dependence of the specific grinding energy on the grinding method is extremely important to know. It is known [3, 4] that the energy consumption is lower when grinding by impact of materials such as coal, quartz, cement, gypsum, rubber, grain, etc., than when crushing by compression and 5-6 times lower than with crushing by impact (ball mill, vibration mill).

Disintegrators - impact mills - are one of the most promising for both industry and laboratory practice. Modern devices of this type have a wide range of productivity: from several kilograms to tens of tons per hour. Disintegrators have several advantages compared to other mills: they are compact, allow grinding materials of a wide range of hardness with little pollution (the latter circumstance is essential in the production of solid-phase materials with structurally sensitive properties), allow varying the specific processing energy of the crushed material by changing rotors or engine speeds [1, 16].

The specific processing energy is the energy that is spent directly on grinding the material. The total energy consumption can be estimated with sufficient accuracy, based on the following ratio:

\[ E = E_i + Q \cdot E_{sp} \]
where: \( E_i \) – idle energy; \( E_{sp} \) – specific grinding energy; \( Q \) – disintegrator performance [1, 15].

Specific tasks are always solved under grinding. In this work, such a task was the mechanochemical production of highly dispersed materials with the required properties from natural raw materials.

**Experimental part**

The mechanical processing of oxide materials was carried out in a laboratory disintegrator DSL-94. The supplied specific mechanical energy was 17.1 kJ/kg in one pass. The specific energy of mechanochemical activation \( E_{MCA} \) was varied by the multiplicity of the passage of the material through the disintegrator. The rotor fingers (contact parts) are made of hard alloys TK-6 and VK-6, which minimizes the contamination of the resulting product by particles of grinding bodies.

The specific surface area of hematite samples was determined by the BET method by low-temperature nitrogen adsorption, the coefficient of variation was not more than 5%; an automatic photosedimentograph of the AFS-2 type was used for determining the dispersed composition.

**Results and discussion**

We have shown previously [1,2] that the background has no appreciable effect on the properties of the silica, and the threshold values of the specific energy of machining, in which the activation effects for silica begin to appear, are \( \approx 50-60 \) kJ/kg (3-fold grinding).

The low sensitivity to the background and the widespread prevalence of silica seem to the authors to be promising for obtaining the required characteristics of oxide powders [13].

Based on spectral studies of crystalline silica before and after machining in a disintegrator [2,7,8], it can be argued that on the surface of its particles (Fig. 1), under the studied conditions, the Si-OH and Si-O-H bonds are broken and the radicals \( \equiv Si \) and \( \equiv SiO \) are formed. However, a pronounced effect is recorded only upon reaching the "threshold" value of the energy of MCA. Similar effects have been observed by other researchers. [10, 14].

The above studies provide a basis for studying the possibility of “grafting” compounds onto the surface of natural silica. This feature opens up the possibility of creating powdered materials based on crystalline silica with a variety of functional purpose and fields of application. [8]

![Figure 1. Model of the surface of silica](image)

Effects arising during mechanical activation in the presence of a surfactant of the following oxide materials: \( SiO_2, ZrO_2, MgO, Al_2O_3 \) were studied as comparison objects.

The results of experiments on mechanochemical processing are presented in Table 1.

**Table 1. The effect of mechanochemical activation in the presence of a water repellent on the properties of oxide powders**

| Type of oxide powder | The specific surface area of the starting material, m\(^2\)/g | The result of mechanochemical exposure in the presence of surfactants* |
|----------------------|-----------------------------------------------------------|---------------------------------------------------------------|
| SiO\(_2\)            | 0,5-0,8                                                   | Significant effect of water repellent is not revealed          |
| ZrO\(_2\)            | 3-8                                                       | Particle size is reduced. The Rebinder effect is observed       |
| MgO                  | 20-40                                                     | The increase in the activity of magnesium oxide in control samples |
| Al\(_2\)O\(_3\)      | 60-80                                                     | Partial hydrophobization of the powder                         |

* Penta-804 tert-butanol and polysiloxanes were used as surfactants.
The data given in Table 1 confirm the earlier assumptions [1] about the minimum size of the specific surface of the starting material at which the hydrophobization effect is possible. On the other hand, the fixing of the Rebinder effect during grinding of zirconium oxide turned out to be important. The Rebinder effect is an adsorption decrease in strength — a change in the mechanical properties of solids due to physicochemical processes that cause a decrease in the surface (interfacial) energy of the body. In the case of a crystalline solid, in addition to reducing the surface energy, it is also important that the crystal has structural defects necessary for the generation of cracks for the manifestation of the Rebinder effect, which then extend under the influence of the environment. Such defects are grain boundaries in polycrystalline bodies [9, 17].

Grains of natural silica have such defects. It was proposed to perform their mechanochemical activation using a solution of polysiloxanes in nephra, which was supposed to provide an adsorption reduction in strength. The results of studying powders fineness obtained after grinding are presented in Table 2. A micrograph of the silica obtained as a result of MCA is presented in Figure 2a. Nearby (Figure 2b), for comparison, a photograph of hydrophobized white soot of the BS-120 brand is shown.

**Table 2.** The effect of grinding mode on the dispersed composition of the obtained silica (d<sub>50</sub> – average particle size)

| Grinding mode                              | Particle size, μm / Particle share, % mass. | d<sub>50</sub> μm |
|--------------------------------------------|---------------------------------------------|------------------|
| direct (1- fold grinding)                  | >63 60,1                                    | 35,65            |
|                                            | 40-63 20,8                                  |                  |
|                                            | 30-40 4,1                                   |                  |
|                                            | 20-30 6,0                                   |                  |
|                                            | 10-20 3,7                                   |                  |
|                                            | <10 5,3                                     |                  |
| direct (3-fold grinding)                   | >63 9,2                                     | 14,19            |
|                                            | 40-63 12,9                                  |                  |
|                                            | 30-40 17,5                                  |                  |
|                                            | 20-30 24,1                                  |                  |
|                                            | 10-20 15,3                                  |                  |
|                                            | <10 21                                      |                  |
| inertial separation                        | >63 0                                       | 14,06            |
|                                            | 40-63 14,7                                  |                  |
|                                            | 30-40 37,3                                  |                  |
|                                            | 20-30 16,0                                  |                  |
|                                            | 10-20 9,6                                   |                  |
|                                            | <10 22,4                                    |                  |
| centrifugal separation                     | >63 0                                       | 6,99             |
|                                            | 40-63 2,6                                   |                  |
|                                            | 30-40 10,2                                  |                  |
|                                            | 20-30 10,7                                  |                  |
|                                            | 10-20 13,2                                  |                  |
|                                            | <10 63,3                                    |                  |
| grinding with a solution of polysiloxanes  | >63 0                                       | 11,02            |
|                                            | 40-63 1,5                                   |                  |
|                                            | 30-40 9,3                                   |                  |
|                                            | 20-30 23,2                                  |                  |
|                                            | 10-20 40,1                                  |                  |
|                                            | <10 25,9                                    |                  |

Analyzing the obtained results, it is worth noting a significant decrease in the average particle size of the obtained powder when grinding it in the presence of a polysiloxane solution. The powder obtained in this grinding mode is inferior to centrifugal separation in particle size, but the regime is less energy-intensive. The share of “large” particles of fractions of 40-63 and 30-40 microns is noticeably reduced. Thus the impact of the Rebinder effect is confirmed when grinding natural silica in the disintegrator in the presence of the corresponding additive components.

**Figure 2.** Microphotographs of finely divided materials:

a) hydrophobized silicon dioxide;

b) hydrophobized white soot (BS-120).
Part of the silica surface was hydrophobized. The retention time of a water drop on the surface of the powder was up to 60 minutes. A photograph of non-wettable silica powder is shown in Figure 3.

![Figure 3. A drop of water with hydrophobized silica particles located on the surface](image)

Thus, a material with the required properties was obtained — natural finely divided silica, the surface of which turned out to be partially hydrophobized. Mechanochemical modification has the perspective as a method for producing highly dispersed powders based on both synthesized and natural oxide materials. The resulting powders can be in demand in reaction powder and other types of concrete requiring highly dispersed fillers.

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