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Obtaining Nanopowders of Metal Oxides from Salts by Means of Mechanochemical Synthesis

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Abstract

The possibility of the mechanochemical synthesis of magnesium and zinc oxide nanopowders has been studied in order to use them as modifying additives for polymers. The process for obtaining nanopowders includes four stages: dehydrating the initial salt, treatment in the planetary mill, washing by means of decantation, and drying. Manganese and zinc chlorides were used as initial salts. Dehydration was carried out at a temperature corresponding to the removal of adsorption and crystallization water as determined by means of TGA. Then the salt was treated in a planetary mill for 2–3 h in the presence of a phase separating agent (sodium nitrite NaNO_2). The treatment process was accompanied by powder dispersing and the mechanochemical reaction between the initial chloride and NaNO_2 salt matrix. The moment of reaction completion was determined basing on pressure changing inside the reaction volume in the course of time. The mixture of oxides and water-soluble salts, obtained as the result of mechanochemical reaction, was washed *via* centrifuging and then the precipitate formed was dried. The resulting oxides were studied with the help of XRD structural analysis, scanning electron microscopy, specific surface measurement by means of BET technique, laser analyzer of particle size. It has been established that the proposed procedure allows obtaining oxide particles with the average size ranging within 60–140 nm.

Key words: mechanochemical synthesis, nanopowders, oxides

INTRODUCTION

For the last years, a growing interest is observed with respect to oxide nanopowders. For today, the most widespread methods for obtaining them include the method of gas-phase reactions, the method of sedimentation and the method of mechanochemical synthesis, plasma-chemical synthesis, explosion method, and vacuum sublimation method. The advantage of the latter consists in a relative simplicity of the equipment used, no requiring for a special processing of initial substances and a possibility for carrying out a one-stage process of synthesis due to simultaneous running of the mechanochemical reaction with oxide formation and its dispersing immediately in the course of mechanical treatment.

A great number of works available from the literature is devoted to studies on the methods for obtaining and properties of various oxides and spinels.

The mechanochemical method resulted in obtaining Al_2O_3 [1], ZrO_2 [2], Gd_2O_3 [3], CeO_2 [4], Cr_2O_3 [5], Nb_2O_5 [6], SnO_2 [7], Fe_2O_3 [8]. As the precursors for performing the mechanochemical synthesis in these works the authors used various salts (more often chlorides), for example CeCl_3 [4], ZrCl_4 [8], both dehydrated, and hydrated, for example $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ [9].

Broad potentials for application of zinc oxide (for example, for improvement strength properties of polythene, as a vulcanizing ingredient in thiocole sealants, for increasing the resistance of polymers against degradation under the action of UV radiation) determine an increased interest of researchers with respect to its synthesis. So, the authors of [10, 11] considered a mechanochemical method for obtaining zinc oxide via performing a solid-phase reaction between ZnCl_2 and Na_2CO_3 with the subsequent heating the product of the reaction to form the oxide.

Our work is devoted to studying a potentiality for synthesizing manganese and zinc oxide nanopowders employing the method of mechanochemical synthesis.

EXPERIMENTAL

As the initial substance we have chosen zinc chloride ($\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$) and manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) due to their availability, relative cheapness and a low-intensity accumulation of adsorption water after drying.

The first stage of the synthesis consisted in the dehydration of the initial chloride is necessary for that that the particles of a salt were not dissolved in their own crystallization water during the grinding process. The dehydration was carried out at a constant temperature equal to 180°C , in a drying oven in ceramic utensils during 3 h. The temperature of dehydration was determined employing a thermogravimetric analysis (TGA) and corresponded to a complete removal of the crystallization water. After drying, we performed weighing the dehydrated salt portion in order to compare with the data resulted from TGA.

Further, we carried out the mechanical treatment of the weighed portion of a salt sample using Fritsch Pulverisette 5 planetary mill in the presence of a phase separator (the frequency of spider rotation amounting to 350 min^{-1}). The milling glass represented a steel drum of 500 mL in capacity, grinding bodies represented steel balls of 10 mm in diameter and 4.08 g in mass, the drum population level being about 45 vol. %, the duration of grinding ranging within 2–3 h). The given mill differs from others in a low volume density of energy, but allows using a gauge pressure and temperature analyzer within a drum.

The processing was carried out employing a “dry” method (without adding any solvents) at a room temperature, in air. Dry technological processes are much more favourable from the economic standpoint and they exclude strong pollution of reaction end products. The conditions for grinding of initial salt and phase separator were varied within a wide range. As the phase separator, we have chosen a strong oxidizer such as NaNO_2 . In the process of mechanical treatment, nitrite plays the role of

an oxidizer and a salt matrix at the initial stage of mechanochemical synthesis.

After the mechanical treatment the obtained powder mixture of water-soluble sodium chloride NaCl and water-insoluble oxide was mixed with distilled water and washed employing a Hettich Rotixa 50 centrifuge (the frequency of rotation being of 3000 min^{-1} , the duration of one cycle being of 15 min) using a decantation method until the neutral pH of washing water was reached. After washing, soluble salts remained in the form of an aqueous solution and then they were poured out, whereas the oxide remained in the form of a precipitate at the bottom of tanks.

Further, the powder obtained was dried at a constant temperature amounting to 80°C during 7 h with the use of a drying oven. At the given temperature, the particles of oxide were not subjected to the process of coagulation, and, moreover there are no phase transformations to occur.

The dried powder was investigated employing the methods of XRD phase analysis, electron microscopy, the analysis of specific surface using the BET technique and the analysis of size distribution for particles.

The XRD structural analysis of samples was carried out with the help of automatic DRON-3 diffractometer (CoK_α radiation). The quantitative phase analysis was carried out via the technique consisting in the approximation of an experimental XRD pattern with a model spectrum. The studies on particle shape and size in the powders was performed by means of Hitachi TM-1000 scanning electron microscope (the accelerating voltage being equal to 15 kV, at 20–10 000-fold magnification, the resolution being of 30 nm, depth resolution amounting to 0.5 mm). The analysis of the specific surface value was performed using the BET low-temperature nitrogen adsorptions technique employing Quantachrome NOVA 1200e apparatus. The analysis of size distribution for particles was carried out using Fritsch Analysette-22 Nanotech laser analyzer of particle size.

RESULTS AND DISCUSSION

In the course of the processing in ball planetary mills, interaction occurs between the

particles of powders and the walls of a drum and grinding bodies. There are two types of interaction to be considered: 1) wearing the powder under friction of a ball against a wall of a container; 2) the absorption of the ball impact energy with its separation from one wall of a drum and striking another wall covered with a thin layer of the substance loaded. In the course of mechanical treatment, not only uniform stirring a salt with the phase separator and changing the sizes of particles occurs, but also the transition from the process of grinding to the process of plastic deformation is observed.

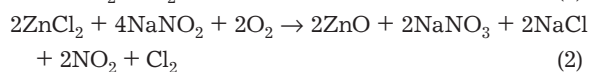
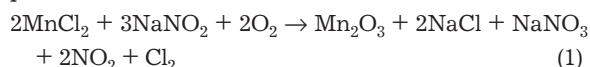
The particles of a material under treatment accumulate the energy in the form of structural defects (dislocations, ionic and atomic vacancies, interstitial ions) those allow lowering the activation energy of chemical transformation. The fields of stress are developed those relax through different channels [12]. First, a part of energy is spent for heating; hence, an intense heat removal is required for avoiding the development of coagulation processes of oxide particles formed. Second, the relaxation goes via grinding and, as a consequence, via the formation of a new surface. This channel of relaxation is the most favourable in order to gain the purpose of our work, since it allows increasing the area of contact between reagents. As a result, the rate of a mechanochemical reaction at the initial stage of solid-phase chemical process increases, which, coupled with the action of a salt matrix provides potentialities for obtaining ultra-disperse oxide particles.

Metal oxides exhibit a high hardness which allows one to obtain highly disperse particles under grinding within the mill.

Substances formed as the result of the mechanochemical reaction are close enough to each other in chemical composition and structure having a plenty of accumulated defects. To all appearance, these circumstances promote the fact that the salt matrix starts to behave as a «wedging» medium. In this case the work of new surface formation under deformation in the course of grinding would decrease as the result of decreasing the free surface energy of particles due to the adsorption of a gas and of the particles of salt matrix.

In the process of the mechanical treatment of initial weighed salt portions the following

mechanochemical reactions are considered to proceed:



As the result of mechanochemical reactions the oxide required and water-soluble salts are formed, brown gas and chlorine are evolved. Since the system is isolated (the drum is tightly closed) the gases evolved create an additional pressure. The treatment process was monitored with the help of a special pressure and temperature gauge, located on the cover of the drum from the inside. The gauge transferred a signal with the information concerning current pressure and temperature to a personal computer (PC) where the signal registered was processed with the help of special software. The graduation was performed in the drum opened under atmospheric pressure.

Basing on the data sent to the personal computer, the graphs of changing the pressure and temperature inside the reaction volume depending on processing time were plotted (Fig. 1). The measured values obtained allow us to judge the course of mechanochemical reactions and the moment of its termination. All the gaseous products are formed only in the course of the reaction. In the process of mechanical activation, the decomposition of NaNO_2 occurs only in the course of its interaction with chloride, which is indicated by a slight increase in pressure (see Fig. 1, d), connected, to all appearance, with the evaporation of residual condensation water in a drum, as well as by a double increase in pressure (see Fig. 1, c).

The use of chlorides and sodium salts as initial reagents is convenient due to the fact that as the result of mechanochemical reactions NaCl is formed which further does not participate in the reaction and plays the role of a salt matrix as a phase separating medium for oxide particles. Hence, a particle of oxide formed is surrounded by an «inert» salt matrix provided that the given phase is in excess. This fact reduces the probability of contact between oxide particles and, hence, results in a decrease of their agglomeration. Thus, varying the loading of initial salts and the conditions of grinding one could achieve the formation of parti-

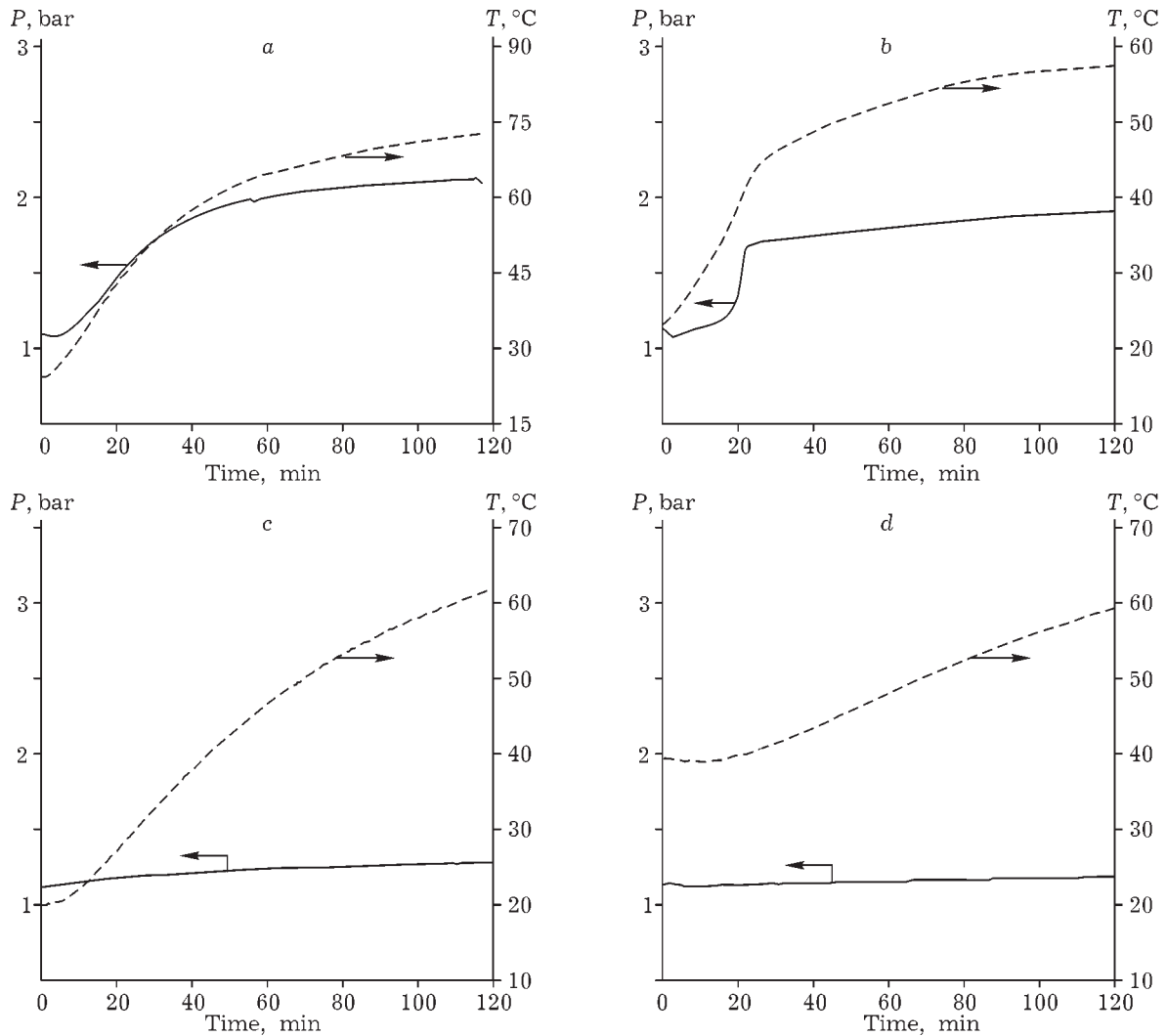


Fig. 1. Pressure and temperature within the drum depending on the treatment duration: *a* - $\text{MnCl}_2 + \text{NaNO}_2$, *b* - $\text{ZnCl}_2 + \text{NaNO}_2$, *c* - NaNO_2 , *d* - ZnCl_2 .

cles with extremely small size, up to the formation of nanosized particles.

In the beginning of the mechanical treatment procedure, a small pressure decrease inside the drum is observed, which could be connected with the oxidation of NaNO_2 by atmospheric oxygen to produce NaNO_3 . The formation of nitrate is also confirmed by the results of XRD phase analysis. Further, the pressure abruptly increases, which could be connected with evolving NO_2 and Cl_2 gases as the result of mechanochemical reactions. In a certain time, intensity of evolving the gases decreases, and for any moment the pressure ceases to grow. This moment could be called the termination of the mechanochemical reaction. The optimum

time of processing was determined basing on data resulting from the analysis of gas evolution.

With the help of scanning electron microscopy (SEM) it has been established, that the particles of zinc oxide ZnO obtained exhibit a needle-like shape with the diameter of 150–200 nm (Fig. 2, *a*). The particles of manganese oxides are of spherical shape being much more inclined to aggregation, whereas the size of aggregates amounts to 800–1000 nm (see Fig. 2, *c*).

According to the data of XRD phase analysis, depending on NaNO_2 excess, either Mn_2O_3 (the size of blocks being of 47 nm), or Mn_3O_4 (21 nm) is formed. The size of blocks for ZnO amounted to 56 nm. The calculation of block size was carried out basing on data resulting

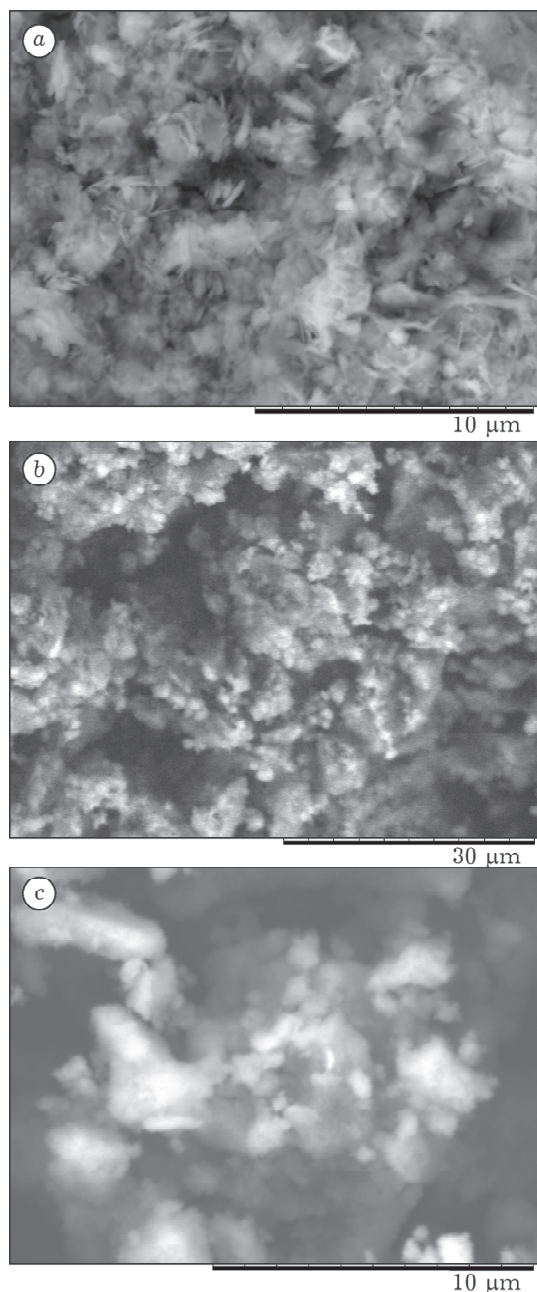


Fig. 2. Microphotographic picture of ZnO (a), Mn_2O_3 (b) and Mn_3O_4 (c) particles.

from the analysis of X-ray line broadening according to the Selyakov–Sherrer formula:

$$D = 0.9\lambda / [\beta_D \cos\theta] \quad (3)$$

Here D is the size of a crystallite; λ is the wavelength of X-ray radiation (1.5178 Å); β_D is the value of physical broadening, connected with the formation of blocks; θ is the diffraction angle for the sample.

In the course of studying unwashed powder we have performed the phase analysis which demonstrated the mass fraction of ox-

ide to be equal to 36 % (the determinate error of measurements being of ± 1 %).

The analysis of the specific surface was performed using the method of low-temperature nitrogen adsorption. For zinc oxide powders obtained $S_{sp} = 7 \text{ m}^2/\text{g}$, which under the suggestion of spherical particles corresponds to the size of 140 nm. This conclusion is supported by the results of the analysis of microphotography pictures obtained employing a scanning microscope. The given size is in 2.5 times higher than the size of blocks calculated from the analysis of XRD line broadening, *i.e.* the oxide obtained, to all appearance, is nanostructured. For Mn_2O_3 , $S_{sp} = 85 \text{ m}^2/\text{g}$, which corresponds to the size of 60 nm. Hence, the microphotography pictures demonstrate strongly aggregated particles. Just as it is for zinc oxide, the size of manganese oxide particles in the powder, determined from the analysis of

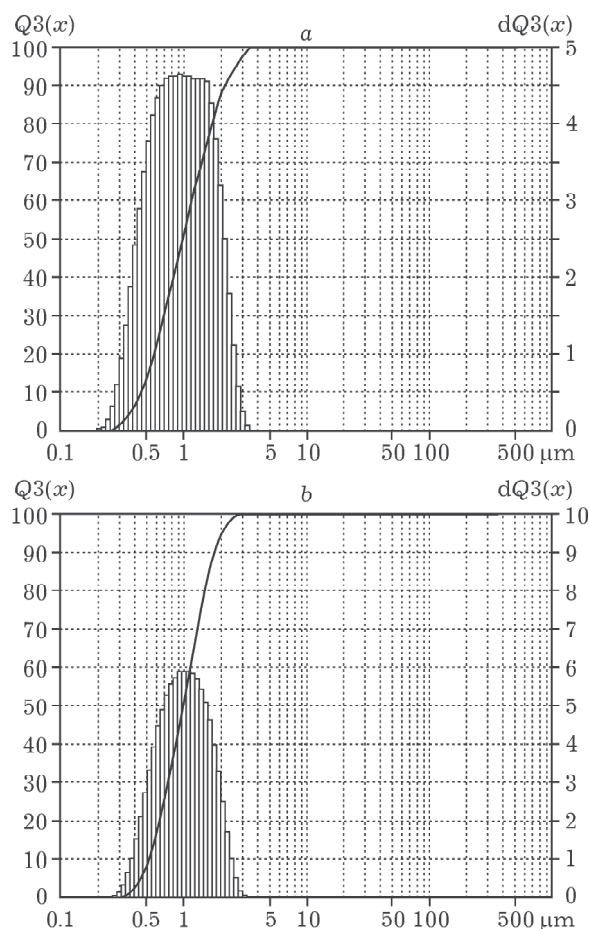


Fig. 3. Size distribution diagram for for of ZnO (a) and Mn_2O_3 (b) particles.

the specific surface is 2.53 times greater than the size of blocks.

The analysis of the size distribution of particles has been carried out. Before the beginning of the analysis a weighed portion of oxide powder obtained was put into a tank with distilled water and was exposed to ultrasound treatment. Further, an aqueous suspension of oxide particles obtained was put into a laser analyzer.

In the course of the analysis, the particles suspended in water begin to aggregate, and the maximum at the distribution curve is shifted to the right. This results in the distortion of the analysis results, since the diagram reflects the size distribution of aggregates rather than separate particles.

As one can see from the distribution diagrams (Fig. 3), the maximum falls on the aggregates with the size of 800 nm, both for manganese oxide, and for zinc oxide.

Basing on the results of the specific surface determination, the analysis of size distribution of particles, SEM and XRD phase analysis one could conclude that oxide powders obtained via the method of mechanochemical synthesis represent nanocrystalline powders with a high level of dispersity.

CONCLUSION

A method of mechanochemical synthesis for obtaining manganese and zinc oxides from the

salts of the metals has been proposed and tested. The essence the method consists in performing a solid-phase reaction between the salts whereby the oxide required and the salt matrix preventing the particle aggregation further washed-out are formed. It is demonstrated that the technique suggested allows one to obtain ultra-disperse powders of oxides, including those less than 100 nm in size. The basic difference of the method developed from the known ones consists in the fact that the processes of synthesizing oxides and dispersing are one-stage ones.

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