Influence of energy parameters on the product of plasdynamic synthesis of ZnO

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Abstract. This paper shows the possibility to synthesize directly the nanodispersed zinc oxide (ZnO) in a hyper-velocity jet of an electric discharge erosive plasma. The investigation results demonstrate how the increase in the supplied energy $W(t)$ influences the phase composition, structure, and dispersity of the synthesized powdered ZnO. Using the X-ray diffractometry and transmission electron microscopy it is shown that the obtained product contains only hexagonal ZnO. It is experimentally established that when $W(t)$ varies from 13.7 to 22.6 kJ, the average particle size of the resulting product increases in the range from 80 nm to 95 nm.

1. Introduction

Due to the unique combination of semiconductor, luminescent, piezoelectric, ferroelectric properties, nanostructured zinc oxide (ZnO) has a wide range of practical applications and is a promising material in the modern industry development [1]. Zinc oxide is a biocompatible, environmentally eco-friendly material with chemical stability and radiation resistance [2-6], which is used in optoelectronics, catalysis, gas sensor manufacturing, energy conversion devices [1, 3, 7-9], as well as in biosensors and biological drug delivery systems means [10-12].

To date, there are many different technologies for obtaining nanodispersed zinc oxide ZnO. The most common synthesis methods are as follows: thermal acetate decomposition, sol-gel method, chemical and hydrothermal synthesis [3, 6, 7, 9]. However, the existing methods for synthesizing ZnO have a number of disadvantages, such as the low process selectivity, the presence of difficult-to-remove impurity compounds, multistage, and the necessity to attract the additional resources.

This paper shows the possibility to obtain nanodispersed zinc oxide by the plasma dynamic method that is based on using a pulsed high-current coaxial magnetoplasma accelerator (CMPA) of an erosive type with a zinc accelerator channel [8]. This method is based on the material crystallization from the liquid phase with a high quenching rate under supersonic sputtering conditions in a gaseous atmosphere. Thanks to the proposed technology, it is possible to synthesize nanodispersed highly crystalline hexagonal zinc oxide with a yield purity of the desired phase up to 100%.
2. Experimental part

The plasma dynamic method is based on the interaction of a zinc-containing supersonic plasma jet with oxygen that occurs during. The main precursor is accumulated due to the zinc barrel erosion during the flow. The plasma jet is initiated in the channel for the plasma structure formation. After passing through the plasma along the accelerating channel, the jet is discharged from the barrel and the pulverized product of the synthesis crystallizes precipitating on the walls of the reactor chamber. At full precipitation, the reactor chamber is opened and the product is collected approximately one hour after the process. Plasma dynamic synthesis provides a short time cycle of accelerator operation (up to 1 ms) synthesis of zinc oxide up to 10 grams and depends on the amount energy supplied, the parameters of the medium in the reactor chamber and the power supply pulse duration.

To estimate the energy input \( W(t) \) effect on the phase composition, structure, and dispersion of the synthesized zinc oxide powder, a series of experiments was performed with a variation energy \( W \) supplied to the accelerator. Figure 1 shows the oscillograms of the discharge current \( I(t) \), the voltage at the accelerator electrodes \( U(t) \) obtained during the experiment. Discharge power curve was built with the current and voltage curves \( P(t)=U(t)\cdot I(t) \). The integration of this curve allows estimating the supplied energy \( W(t) \). It can be seen from the \( W(t) \) curves that the amount of energy supplied varies and value to \( W_1=13.7 \text{ kJ} \) (a); \( W_2=19.1 \text{ kJ} \) (b); \( W_3=22.6 \text{ kJ} \) (c), respectively. The entire process takes the order of \( t_{imp}=400 \mu \text{s} \). It can be seen from the oscillograms that the value of the supplied energy increases with increasing discharge current at \( I_m=95.0 \text{ kA} \), the value \( W=13.7 \text{ kJ} \), while for \( I_m=110.6 \text{ kA} \) this value increases and reaches \( W=22.6 \text{ kJ} \). Thus, the voltage at the accelerator electrodes is practically unchanged in the experiments and thus, the value of the supplied energy \( W \) depends only on the discharge current flowing at the accelerator electrodes \( I_m \).

![Figure 1](image1.png)

**Figure 1.** Typical oscillograms of the current of the power supply \( I(t) \), voltage at the accelerator electrodes \( U(t) \), curves of the discharge power in the accelerating channel \( P(t) \) and the input energy a) \( W_1=13.7 \text{ kJ} \); b) \( W_2=19.1 \text{ kJ} \); c) \( W_3=22.6 \text{ kJ} \).

After the experiment, the product of plasma-dynamic synthesis was collected after some time from the walls of the reactor chamber and without any preliminary preparations was studied by scanning electron microscopy using the Hitachi TM3000 microscope with an accelerating voltage of 15 kV, in a mode of inverse electron reflection COMPO and using a system with electronic and focused ion beam Quanta 200 3D. In addition, the material was studied on a Shimadzu XRD 7000S X-ray diffractometer (CuK\(\alpha\)-radiation) with a Shimadzu CM 3121 monochromator, the results of X-ray analysis from
which were processed in the Crystallographica Search-Match program. The transmission electron microscopy was carried out using a Philips SM 12 microscope to analyze the structure and size of the obtained plasma-dynamic synthesis material with an accelerating voltage of 100 kV.

3. Results and discussion

Figure 2 shows scanning electron microscopy (SEM) images of the product of plasmodynamic synthesis as a function of the energy supplied with the smallest (a), medium (b), and maximum (c). Judging by the dimensional rulers, the product has submicron and ultramicron sizes. On the whole, product images show that the material is highly agglomerated and is presented in the hexagonal particles form. Comparison of SEM images clearly shows that an increase in the energy \( W \) is accompanied by the formation in the synthesized product of single crystals of submicron sizes of the correct shape with increasing particle sizes.

![Figure 2](image)

Figure 2. SEM images of synthesized materials a) \( W_1 = 13.7 \) kJ; b) \( W_2 = 19.1 \) kJ; c) \( W_3 = 22.6 \) kJ.

To determine the phase composition of synthesized powders, X-ray diffraction analysis was used. Figure 3 shows XRD-patterns of powders obtained at different supplied energy values. The analysis of the diffraction obtained showed the proximity of the synthesized powders to the structural model of the \( \text{ZnO} \) zinc oxide phase (card number 36-1451, hexagonal system, \( P63mc \) space group (no. 186), crystal lattice parameters \( a = b = 3.24982 \) Å, \( c = 5.20661 \) Å). However, in the diffractogram of the material synthesized at a value of the supplied energy \( W = 13.7 \) kJ (figure 3a), a small intensity peak was observed at the interval \( 2\theta = 43\div44 \) degrees, which refers to the most intense maximum of the pure zinc metal phase \( \text{Zn} \) card 4-831, hexagonal system, space group \( P63/mmc \) (no. 194), the parameters of the crystal lattice are \( a = b = 2.665 \) Å, \( c = 4.947 \) Å. However, in view of the high intensity of the reflexes of the synthesized product on the diffractogram, it is not possible to estimate the percentage of the phases, so we assume the presence of the \( \text{Zn} \) phase at trace level. In addition, diffraction of the synthesized material is shown on the isolated part of the diffraction pattern, but after annealing at a temperature of 800°C in atmospheric conditions without holding the maximum temperature for a time, with a heating rate of 14°C/min. A comparative analysis of the initial product and the material after annealing suggests that the metallic zinc at this temperature melts and undergoes oxidation, passing into zinc oxide, so after annealing on X-ray diffraction, only the phase of zinc oxide is identified.

A comparative analysis of the X-ray diffraction patterns of products obtained at different values of the energy input allows us to conclude that at a relatively low value of \( W \), an impurity pure zinc metal phase is found in the product, but even at an energy level of \( W_2 = 19.1 \) kJ and more, the synthesized product consists of 100% \( \text{ZnO} \). Thus, at a certain level of the supplied energy, it is possible to synthesize pure zinc oxide without additional additives.

The results of transmission electron microscopy of three products of plasma-dynamic synthesis are shown in figure 4. By light-field and dark-field TEM images, it is seen that with a relatively low energy input \( W_1 = 13.7 \) kJ, practically all particles have a rounded shape. With an increase in energy to...
$W_2=19.1$ kJ, one can observe an increase in the particle size and the acquisition of more rigorous geometric shapes by them. Such a difference in the shapes of particles obtained under different energy conditions can be explained by the higher temperature of the synthesis process with a high level of energy supplied and, as a result, the particles shape becomes more even. The identified phase of zinc oxide from x-ray diffractograms has a hexagonal lattice structure, and comparing these data with the transmission electron microscopy data it can be concluded that the particles of regular shape are hexagons, which are rotated in different directions in the photographs (regular hexagon, lateral rectangular side).

![Figure 3. Diffractograms of the obtained powdery products of plasmodynamic synthesis](image)

The patterns of electron microdiffraction on selected regions (particle clusters on TEM images) (SAED) have a point-circular character. All reflexes with sufficiently high accuracy of determination of interplanar distances correspond to the structural model of ZnO, determined by XRD analysis. Dark-field TEM images clearly represent the single-crystal obtained product structure of plasmodynamic synthesis. In figure 4, histograms of the particle size distribution are plotted in parallel to each TEM analysis.

The histograms of the particle size distribution were obtained from several clear-field TEM images (a minimum of 100 particles in each experiment). The average particle size in the experiments varies and is at a minimum energy of 60 to 100 nm, with an average energy of 60 to 140 nm, and at the maximum value of the energy input, the distribution range increases significantly and is from 40 to 200 nm. It is also worth noting that in the first case the normal law of particle size distribution (Gaussian distribution) takes place, while for the larger energy the resulting distribution can be attributed to Poisson (discrete) distribution. Thus, the analysis of the particle size distribution as a function of the amount of energy supplied showed that with increasing W the particle size in the plasma-dynamic synthesis product increases and the range of particle size distribution increases.
4. Conclusion
The work shows the possibility of obtaining a highly disperse monocrystalline zinc oxide powder by the plasma-dynamic method using a system based on a coaxial magnetoplasma accelerator with a zinc accelerator channel.

During the study of the influence of the supplied energy on the phase composition, structure, and dispersity of the synthesized powdered ZnO, it was established that an increase in W in the range from 15 to 23 kJ is accompanied by a slight increase in the average crystallite size and broadening of the particle size distribution range. It has been revealed that in the case of a lack of supplied energy, unreacted zinc metal remains in the product of plasmodynamic synthesis, but even with an increase of this value to 19.1 kJ or an annealing of 800°C, it is possible to obtain a product with 100% monocrystalline hexagonal nanodispersed zinc oxide ZnO.

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