Influence of the type of electric discharge on the properties of the produced aluminium nanoparticles

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Abstract. The effect of the method of aluminum nanopowder production on the aluminum products with water reaction is described. It has been established that the interaction of aluminum nanopowder prepared by the electric wire explosion, the phase composition of the reaction products mainly consists of boehmite (AlOOH) and has a fibrous structure. Therefore, boehmite (AlOOH) can be used for modification of polymer membranes. The modified membranes can be used as water treatment from the impurity of formed true solutions according to adsorptive mechanism, and from colloidal nanometer and micron particles according to the mechanism of mechanical separation of particles depending on sizes.

Keywords: aluminum nanopowder, electrical explosion, modification of membranes

1. Introduction
Modern methods of producing nanofibrous aluminum oxyhydroxide (AlOOH) sufficiently diverse due to their use in the synthesis of various precursors based on aluminum, such as salts or in the form of metal powders [1–5]. The basis of these methods is the chemical synthesis of aluminum oxyhydroxide. The most common method of cooking is aluminum oxyhydroxide precipitation from solutions of salts of aluminum or aluminate solutions. More commonly, the salts used as starting chlorides, nitrates and sulfates of aluminum. With this method of producing aluminum oxyhydroxide, its composition and properties depend on the pH and temperature of the reaction medium. The reproducibility of this method is relatively low, which affects the properties of the resulting product. One way to obtain aluminum oxyhydroxide with desired properties is aluminogels hydrothermal treatment. The advantages of this method are the possibility of choosing the parameters (t, P, τ), providing the properties of good reproducibility and high quality product. A disadvantage of this method is the necessity of using high temperature and pressure, which affects the final product cost.

There are direct methods of producing aluminum oxyhydroxide, which are based on the oxidation reaction of aluminum metal. The main problem of these methods is to activate the surface of aluminum metal. It is therefore of interest to develop technologies for the production of aluminum with a thin oxide (protective film). There are methods of producing, allowing to obtain an active alumina capable of easily reacting with water to form aluminum oxyhydroxide by reacting:

These methods are the method of electric wire explosion (EWE) and the method of pulsed electric discharge (PED).

The purpose of this study is to compare the products of oxidation of aluminum, obtained by EEW and PED with water.

2. Materials and methods
In this work was used nanofibers of aluminum oxyhydroxide, which were obtained by the two methods:
1. The reaction of water and nanodispersed aluminum particles preliminary generated in the argon atmosphere by electric wire explosion.
2. The reaction of water and aluminum particles generated directly in water by electric discharge.

The main difference of these methods are difference of a precursors and type of discharge.

The first method is basing on the interaction of water and nanodispersed aluminum particles generated by electric wire explosion in an argon environment. Figure 1 a shows the scheme of this method.

This technology allows getting the particles of spherical shape with normal logarithmic distribution of particles by sizes (Figure 1b). The disparity of powders can be easily regulated by the change of energy applied to the wire.

The facts that there is no solid protective layer on the aluminum powders generated by this method, and the content of active metal changes in time to 100 % and less are very promising in comparison with metallic aluminum. In spite of a low content of active aluminum, the powders continue to react with water actively.

This method provides a nanosized powder of aluminum, but aluminum oxyhydroxide. So the next step was to carry out the oxidation of aluminum nanopowder with water at a constant temperature of 60 °C for 8 hours [6]. Only when the reaction of water with aluminum nanopowder aluminum oxyhydroxide can be obtained, whose the electron micrographs are shown on Figure 3b.

The second approach represents a generation of nanopowders directly in water. For this purpose, we used electric discharge technology [7]. The principle of this method is the following: two electrodes are placing in the chamber with the particular geometry. The space between the electrodes were filling with water and some pieces of aluminum shavings. When high voltage pulse were supplying to the electrodes, multiple micro discharges were generating between the shavings. Under the action of these micro discharges, the metal was destructing and thrown out in water as the small particles. Figure 2 shows the scheme of this method.
This method allows obtained aluminum oxyhydroxide by one step. The electron micrograph of the resulting product are shown on the Figure 3b.

The all sample of the nanofibers of aluminum oxyhydroxide content of active (metallic) aluminum, phase content, area of specific surface and particle shape were determined. The phase composition of the samples was examined by X-ray diffraction using a Shimadzu XRD-7000 diffractometric at the angular range $2\theta$ 10 – 100° and scanning rate of 1 deg min$^{-1}$. The specific surface area of aluminum nanoparticles were measured by the BET technique on Sorbtometer-M. The size and shape of particles were determined using the electron microscope. Morphological structure of all nanofibers were studied on transmission electron microscope - JEM-2100F, Japan.

The heat effects and changes in the phase composition during gradual heating of the samples in an inert argon atmosphere were determined on an SDT Q600 – Simultaneous TGA/DSC/DTA analyzer at 0 – 1000 °C.

3. Results and Discussion
Figure 3 shows the electron micrographs of products of oxidation of metallic aluminum with water, obtained by the two methods described above.

![Figure 4. The electron micrographs of products of the reaction of aluminum with water: a – by the electric explosion; b – by the electric discharge.](image)
It is seen that the product obtained from aluminum nanopowder has a fibrous structure and product obtained by the electrical discharge method is part of a fibrous structure with the particles of round shape - aluminum metal. The results of the products analysis of this reaction are shown in the table 1.

| Type of products                  | Phase composition [%] | Specific surface [m²/g] | Particle shape                      |
|-----------------------------------|-----------------------|-------------------------|------------------------------------|
| Products generated by electric wire explosion | AlOOH – 85,0          | Al(OH)₃ – 10,0          | 175,5                              |
|                                   | Al₂O₃ – 4,0            | Al – 1,0                | fibers                             |
| Products generated by electric discharge method | AlOOH – 6,0           | Al(OH)₃ – 90,0          | 69,3                               |
|                                   | Al₂O₃ – 2,0            | Al – 2,0                | crystals of indefinite shape and plate-shape particles |

Products obtained from electric explosion powders contain mainly nanofibers about 5 to 8 nm. in diameter. Al(OH)₃, Al₂O₃ and Al were in a small amount. The specific surface of nanofibers changes over a wide range, more than single-order and it is determined, basically, by depressiveness of an initial powder, the contents of active metal and initial water temperature.

The products obtained by electric discharge in water contain the crystals of an indefinite shape and very thin plates. The phase structure of these products includes basically Al(OH)₃. In some tests AlOOH, Al₂O₃ и Al are registered. The specific surface of the products depends more often on pH and water temperature.

We studied the behavior of the products reaction obtained by the different methods under heat by the method of the combined thermal analysis, using SDT Q600 Analyzer. Figure 5 demonstrates the results of analysis.

![Thermograms of the products.](image)

**Figure 5.** Thermograms of the products.
It is evident from the thermograms that the curves of weight loss and the character of phase transitions at the temperature range below 500 °C differ essentially. These differences are the result of phase composition of analyzed products. The AlOOH phase passes into Al$_2$O$_3$ phase at 300 – 400 °C with conservation of fibrous structure. Thus, Al$_2$O$_3$ fibers get more precise shape. The specific surface increases on 20 – 25 wt. %. The Al(OH)$_3$ phase passes in oxides in wider temperature interval. So the crystals of long shape are formed.

4. Conclusion
It was demonstrated that the phase AlOOH are composed of the product by oxidation reaction aluminum nanopowder obtained by EVD, with water, and the products obtained during electroerosion composed of Al (OH)$_3$. The specific surface area of AlOOH are greatest, which makes this material a promising treatment methods for sorption of various media [8], as well as the possibility of its use as a modifier for polymeric membranes and as the carrier for catalysts [9].

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