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Effect of Al/AlN Deagglomeration on the Formation of a Modifying Porous Coating on Polymeric Fibres

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Abstract

Using dynamic light scattering technique, studying the destruction process were performed for the agglomerates of electro-explosion aluminium nitride nanopowder composition Al/AlN under ultrasonic dispersing in isopropyl alcohol. The average size of the initial agglomerates amounts to ~5.4 μm. It has been demonstrated that under the conditions of dispersing under investigation the initial agglomerates are disintegrated to produce a particle size of about 0.5 μm. No destruction resulting in primary particles of 40–80 nm in size is observed. It is demonstrated that the deagglomeration exerts a considerable effect upon the chemical reactivity of the aluminium nitride nanopowder composition in the reaction with water. It has been established that the size of the precursor particles exerts a substantial effect on the formation of a modifying nanostructured porous coating on polymeric fibres and on adsorption properties of the fibrous sorbent based the mentioned coating.

Key words: deagglomeration, nanopowder, modification, porous coating, adsorption

INTRODUCTION

The use of nanodispersed powders as additives in making different functional materials is of current importance; however the standalone usage of nanoparticles is difficult. Having such pronounced features, as high surface energy and chemical reactivity, the nanoparticles tend to form agglomerates with the sizes ranging from several micrometres to several dozens of micrometres already in the course of synthesis thereof [1, 2]. Wherewith the decrease in the size of primary particles the agglomeration level of nanopowders increases [3]. As a consequence, the nanoparticles lose their individual properties, and, moreover, problems arise concerning the making of materials on this base, which problems are associated with the uneven distribution of the agglomerates in the bulk or on the surface of polymeric materials [3, 4].

Of particular interest is the formation of the modifying sorbent layers resulting from nanoparticles or of the reaction products thereof on the surface of polymeric fibres or membranes [3, 5–10]. The sorption efficiency depends on the amount of the modifying phase in the sorption material, as well as on uniformity (continuity) of a modifying layer on the surface of the fibres. In turn, the structure of the modifying layer (thickness, continuity) is determined by the size of the agglomerates of the precursor and by the uniformity of distribution along the fibre. It is obvious, that decreasing the agglomeration level of a precursor in the case of modifying the polymeric fibres should result in obtaining a more thin uniform coating.

There are different methods known for the deagglomeration of nanoparticles involving the use of encapsulating polymers, the passivation of nanoparticles by means of stabilizing the colloidal solutions thereof [11–13], *etc*. However, owing to strong interaction between the surface of the particles and the stabilizing agent, a decrease in the reactivity of the nanoparticles is observed. By the contrast with the other technologies of dispersing, the ultrasonic (US) treatment does not require for using additional chemicals, it is simple in equipment design and makes it easy to move from laboratory research to industrial production [14, 15].

The aim of this work consisted in studying the influence of the duration of suspension ultrasonic treatment upon the agglomerate size of the electro-explosion aluminium nitride nanopowder composition Al/AlN, on the macrokinetic parameters of hydrolysis thereof, on the particle size of the resulting aluminium oxyhydroxide and on the homogeneity of its distribution over the surface of the fibres, as well as in studying the sorption properties of the fibrous sorbent modified.

EXPERIMENTAL

As a subject of inquiry we used Al/AlN nanopowder (30 mass % of Al and 67 mass % of AlN) with the specific surface value equal to 16 m^2/g. In the course of the electric explosion of aluminium in a nitrogen atmosphere one observe the particles to form those represent aluminium core with a shell of AlN. The surface of the particles is coated with amorphous oxide film, whose the calculated thickness is equal to 6 Å, the content of the oxidized phase amounting to ~3 mass % [16]. The primary particle size inherent in the Al/AlN nanopowder was calculated basing on TEM images obtained by means transmission electron microscopy technique with a JEM 100 CXII electron microscope (JEOL).

The procedure of dispersing the suspension Al/AlN (1 mass %) was performed in a constant-temperature environment at 20 °C using an UZG 13-0.1/22 ultrasonic disperser, the duration of the experiment ranged within 5–60 min, the radiation power was equal to 100 W, the ultrasonic wave frequency being of 22 kHz. The suspension was prepared in isopropyl alcohol with no stabilizers (dispersants) because the presence of extraneous substances could exert an influence upon the hydrolysis of aluminium nitride nanopowder compositions and upon the sorption properties of the resulting sorption material. The size distribution of Al/AlN agglomerates was investigated using a CPS BS-24000 disc centrifuge by means of dynamic light scattering technique. Experimental data obtained were processed using original Disc Centrifuge Control System (DCCS) software.

The chemical reactivity of Al/AlN samples was determined from the reaction with water according to the procedure described in [16]. The investigations concerning the morphology and uniformity particle distribution for the nanostructured aluminium oxyhydroxide over the fibres of the polymeric matrix was performed by means of scanning electron microscopy with the use of a 50 EVO (Carl Zeiss, Jena, Germany) and Philips SEM 515 of scanning electron microscopes.

In order to obtain the fibrous sorbent, we used cellulose acetate polymeric fibres with a diameter of 1–3 μm, whereon we applied an aqueous suspension of Al/AlN treated with ultrasound during 45 min, with the further hydrolysis of the nanopowder to form and adhesively fix the aluminium oxyhydroxide particles onto the fibres of the carrier in the amount ranging within 24–27 mass % for all the samples.

The absorption capacity of the fibrous sorbent samples was studied by the example of anionic dye eosin ($C_{20}H_6O_5Br_4K_2$) under dynamic conditions [17]. For this purpose, we passed the adsorbate solution with the concentration of 25 mg/L through the material layer with the working surface area of 13 cm^2, at a flow rate equal to 20 cm^3/min (0.025 cm/s). The concentration of the dye in the solutions was determined using a Spekol 1300 spectrophotometer in a quartz cell with an optical path length $d = 10$ mm at the maximum of the absorption band at the wavelength $\lambda = 490$ nm.

The antimicrobial activity of the fibrous sorbent was examined under dynamic conditions in the course of passing the model water contaminated by microorganisms through the samples of the material with the working surface area amounting to 13 cm^2. The filtration rate was maintained to be 144 cm^3/min (0.18 cm/s) in the course of the entire experiment. The investigations were performed by the example of the bacterial culture *Escherichia coli* 1257 (*E. coli*) ac-

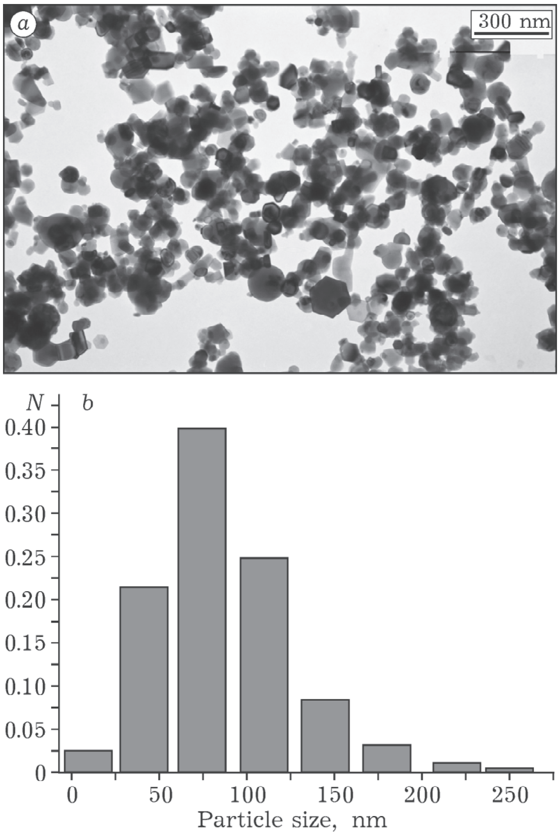

Fig. 1. TEM image (*a*) and number-average particle size distribution (*b*) for nanopowder Al/AlN.

cording to the technique described in [7, 18]. The concentration of microorganisms in the model solution amounted to $1.3 \cdot 10^5$ of colony forming units per 1 mL of the solution (CFU/mL).

RESULTS AND DISCUSSION

The aluminium nitride composition powder is presented by the primary particle of 40–80 nm in size (Fig. 1). Owing to a high chemical reactivity of the Al/AlN nanopowder the ultrasonic processing thereof was carried out in an isopropyl alcohol environment under constant-temperature conditions to avoid hydrolysis reaction during the dispersing procedure.

The initial particles of the aluminum nitride compositions are presented by agglomerates with a prevailing size larger than 5 μm (Fig. 2, curve *1*). In the course of ultrasonic processing the suspension during 5–15 min the initial agglomerates are destructed with the formation of large fragment with the size ranging within 1.2–2.3 μm. Furthermore, within the size region of 0.5 μm there appears a “shoulder” (see Fig. 2, curves *2*, *3*). Increasing the treatment time up to the range of 30–60 min resulted in the destruction of the initial agglomerates and bimodal particle distribution to occur with the maxima at 1.2 μm and 0.5 μm. In this case, the mass fraction of the particles with the size of 0.5 μm exhibits an increase (see Fig. 2, curves *4*–*6*). In the case of the suspension ultrasonic treatment during 60 min one can observe decreasing the mass fraction of agglomerates with the size equal to 1.2 μm and, accordingly, an increases the contribution of particles with the size ranging within 0.3–0.6 μm (see Fig. 2, curve *6*). It should be noted that the further increase in the duration of ultrasonic exposure does not result in a noticeable changing in the nature and distribution of the particles and breaking the agglomerates down to the size of primary particles (40–80 nm).

Reducing the size of the agglomerates in the course of ultrasonic dispersing the suspension of Al/AlN promotes increasing the chemical reactivity and changing the macrokinetic parameters of nanopowder hydrolysis. It is known [16] that Al/AlN reacts with water at a room temperature, whereas at 50–60 °C the reaction proceeds rapidly with a high level of gas evolution and heat generation. The hydrolysis reaction is preceded by an induction period wherein there is the hydration and dissolution of an oxide film occurring, and no considerable changing the pH value. It can be seen

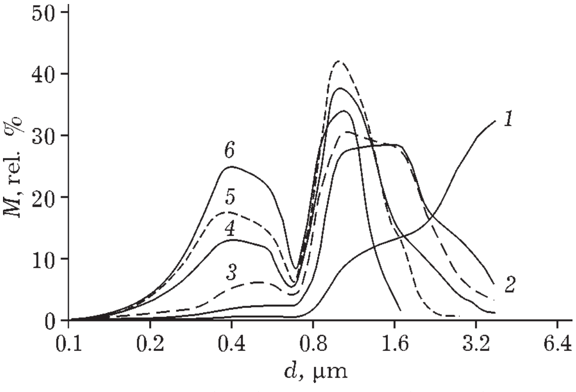

Fig. 2. Mass-average distribution for initial (*1*) and sonicated (*2*–*6*) Al/AlN particles. The duration of ultrasonic treatment, min: 5 (*2*), 15 (*3*), 30 (*4*), 45 (*5*), 60 (*6*).

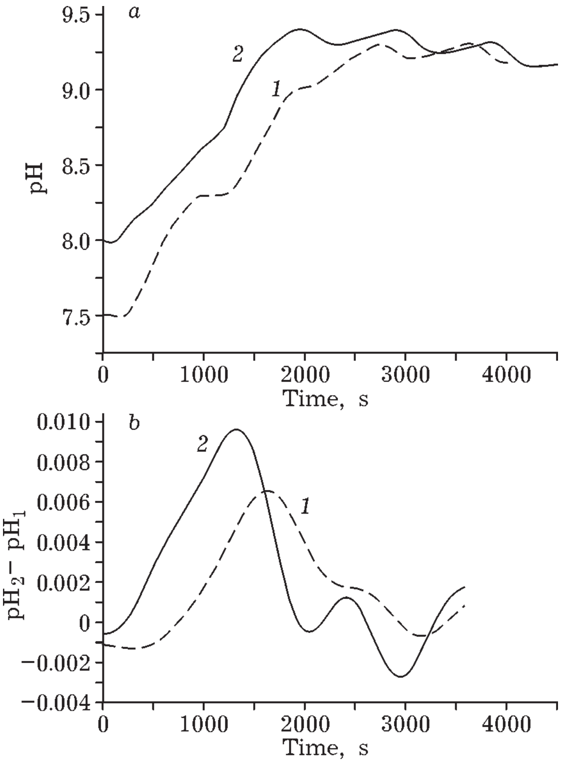

Fig. 3. Integral (*a*) and the differential (*b*) kinetic curves for varying the pH value in the course of Al/AlN nanopowder hydrolysis: *1* – initial, *2* – sonicated.

(Fig. 3, *a*) that the kinetic curves of change the pH of the reaction mixture exhibit an S shape inherent in topochemical processes, whereas the differential curves exhibit two maxima (see Fig. 3, *b*), which could be connected with structural hydrolytic features of Al/AlN particles. The hydrolysis of Al/AlN occurs *via* two macrokinetic stages: the first stage represents the hydrolysis of the AlN shell accompanied by the evolution of ammonia and increasing the pH value in the system. At the second stage aluminum core reacts with water with the evolution of hydrogen [16]. Decreasing the average size of the agglomerates in the course of ultrasonic treatment during 60 min results in decreasing the induction period from the value of 6.7 min for the initial powder to 0.2 min for the particles with the average size ranging within 0.5–1.2 μm, wherewith the reaction rate increases (see Fig. 3, *b*).

The agglomerated Al/AlN nanopowder treated by ultrasound was used as a precursor for modifying the fibres of a polymeric nonwoven material. The electron microscopic examination of the samples of the modified fibrous sorbent demonstrated that the hydrolysis of the initial agglomerated Al/AlN powder in the presence of fibrous substrate results in the formation of aluminum oxyhydroxide particles of 10–15 μm in size (Fig. 4 *a*, *b*), those are located in the inter-fibre pore space of the polymer material. The sonication of Al/AlN suspension during 5 min results in the destruction of the initial agglomerates, which promotes reducing the size of the hydrolysis products down to 1–5 μm (see Fig. 4, *c*). Dispersing the precursor suspension for 30 min results in the formation of the modifying porous coating on the polymeric fibres, the mean particle size being reduced down to 0.2–1.0 μm (see Fig. 4, *d*), whereas for 45 min of the dispersing procedure this parameter is equal to 0.2–0.5 μm (see Fig. 4, *e*, *f*). In addition, there are areas of uniform porous coating the polymer fibres by nanosized aluminium oxyhydroxide particles observed (see Fig. 4, *d*).

Thus, in the course of applying the aqueous suspension of Al/AlN treated with ultrasound to a fibrous substrate, the nanopowder particles are coating the polymeric fibres by a relatively homogeneous layer, whereas aluminium oxyhydroxide formed during the hydrolysis forms smaller agglomerates immobilized on the fibres. The deagglomeration of the precursor promotes the aluminium oxyhydroxide particle size to be reduced down to 0.2–0.5 μm with the formation of a uniform porous coating on the polymer fibres.

In order to study the sorption properties of the modified material we investigated the dynamic adsorption of eosin and of the test bacterial culture *E. coli*. It has been demonstrated that decreasing the particle size of the modifying coating with the uniform distribution over the surface of the polymeric fibres results in increasing the sorption capacity level with respect to eosin from 6 to 25 mg/g and in the duration of the protective effect from 5 to 12 min (Fig. 5). Taking into account a small size of the dye molecules, a high surface area and porosity of the hydrolysis products, it can be assumed that increasing the duration of the protective effect could be, to all appearance, caused by kinetic factors. In the case of when

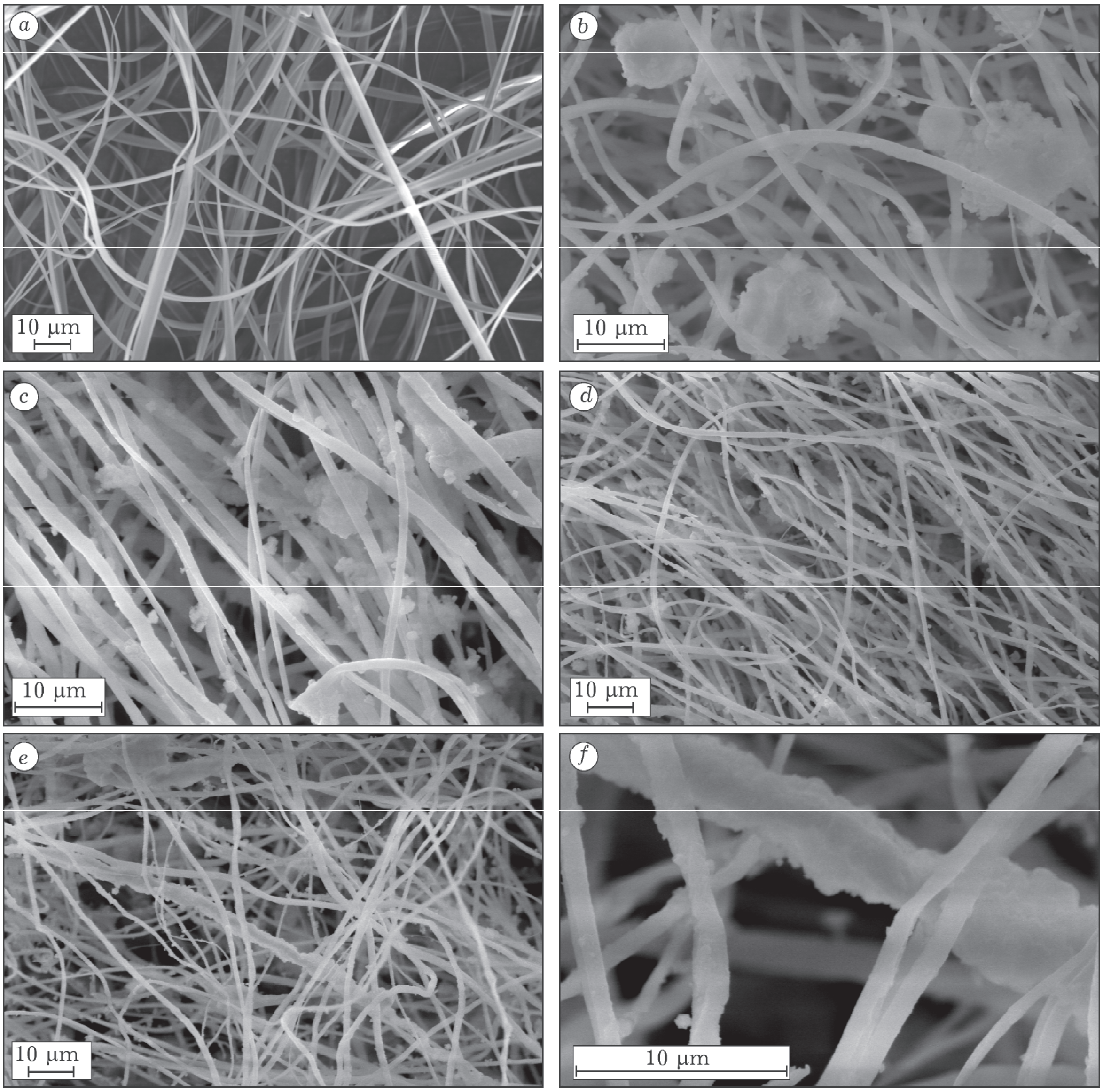

Fig. 4. SEM images of the initial polymeric (*a*) and modified fibres with no ultrasound treatment (sonication) of the suspension (*b*) and those ultrasonically treated during 5 (*c*), 30 (*d*) and 45 min (*e*, *f*).

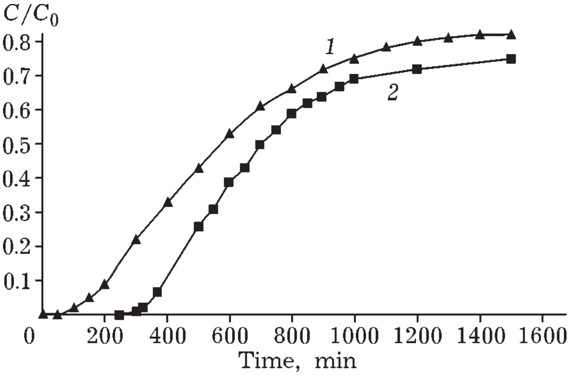

Fig. 5. Dynamic curves for eosin adsorption by the fibrous sorbent modified with the particles of 10–15 μm size (*1*) and with a uniform porous coating (*2*). C_0, C stand for the initial and the current concentration of eosin.

a relatively thin uniform modifying layer consisting of aluminium oxyhydroxide is formed, the amount of readily available surface adsorption sites increases to a significant extent as to compare with the case of large agglomerates, whereto the diffusion of the dye molecules is difficult, which is a determining fact for the rate of adsorption.

The sorption efficiency of *E. coli* by the samples of the fibrous sorbent obtained without sonication of the precursor was equal to 100 % at the load on the filter equal to 10^7 CFU/cm^2. Further, in the course of passing the model contaminated through the filter, the filtrate exhibited an effect of trace bacterial breakthrough. At the same time, the fibre samples with a uniform porous sorbent coating of polymeric fibres withstood a load greater than 10^{10} CFU/cm^2 with 100 % adsorption efficiency with respect to microorganisms. Further increasing the microbial load resulted in filling the pore space of the sorption material by a biological mass, in increasing the dynamic resistance and in significant reducing the filtration rate.

Thus, the ultrasonic treatment of the powder suspension results in the destruction of agglomerates and in decreasing the average particle size, which affects the macrokinetic parameters of the reaction of Al/AlN hydrolysis. The deagglomeration of the precursor allows obtaining a fibrous sorbent with the uniform distribution of aluminium oxyhydroxide nanoparticles over the surface of polymeric fibres, which provides the adsorption capacity level to be increased.

CONCLUSION

1. The results of the investigation performed demonstrate that the nanopowder Al/AlN obtained using the technique of electrical explosion represents mainly by agglomerates larger than 5 μm. The deagglomeration of the Al/AlN powder by means of ultrasonication during 60 min resulted in a successive disintegration (crushing) of the initial agglomerates into the fractions with an average particle size of 1.2 and 0.5 μm. The intense destruction of initial agglomerates can be observed during the first 30 min of ultrasonic exposure, whereas the further sonication results only in insignificant decreasing the contribution of the 1.2 μm fraction and slight increasing the contribution of 0.5 μm fraction. It should be noted that in the dispersing conditions under investigation there is no destruction of the agglomerates occurring to form primary particles with the size of 40–80 nm.

2. The physicochemical properties of Al/AlN and its hydrolysis products are to a great extent determined by the agglomeration level of the initial nanopowder. The deagglomeration of nanopowder results in changing the chemical reactivity thereof, increasing the hydrolysis rate of Al/AlN, and decreasing the particle size of the products from 10–15 to 0.2–0.5 μm. The deagglomeration provides a uniform distribution of the precursor particles and, consequently, the uniform distribution of hydrolysis products on the surface of the fibres in the form of a porous coating in the course of modifying the polymeric fibres.

3. The formation of the uniform porous coating with the thickness ranging within 0.2–0.5 μm on the surface of polymeric fibres provides the surface sites to become available, which results increasing the sorption capacity level of the material with respect to eosin up to 25 mg/g, and with respect to bacteria *E. coli* up to 10^{10} CFU/cm^2.

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