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Structure and Texture of Oxyhydroxides Formed by Oxidation of Nanodispersed Aluminum with Water

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Abstract—Aluminum oxyhydroxides were prepared by oxidation with water (55°C) of nanodispersed aluminum powders obtained by electric explosion of conductors in argon, nitrogen, carbon dioxide, and their mixtures. The structure and texture of aluminum oxyhydroxides were studied using methods of thermal desorption of nitrogen, derivatography, electron microscopy, and X-ray phase analysis.

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Nanotechnology is today one of priority fields in developed countries. Nanomaterials are used in composites for preparing ceramics, catalysts, and sorbents, as molecular sieves, aerogels, and materials for solar batteries and fuel cells, and also in magnetic tomography, optoelectronics, photonics, microbiology, and medicine. The use of nanomaterials as sorbents is based on their high sorption ability toward various kinds of substances [1–5].

One of procedures for preparing nanomaterials is electric explosion of conductors (EEC) [6]. The first studies and semicommercial production of submicrometer aluminum powders by this method were performed in an inert gas (argon) atmosphere, with the subsequent passivation of the particles by admitting air into the explosion chamber. Aluminum nanopowders exhibit unique properties compared to submicrometer powders and, the more so, to bulk materials. For example, aluminum nanopowders react with water even at room temperature, and even slight (to 40–50°C) heating of the reaction mixture results in vigorous hydrogen evolution and self-heating of the system [7–12]. Oxidation of aluminum with water yields a mixture of finely dispersed products (aluminum oxyhydroxides) whose composition and properties strongly depend on the synthesis conditions: oxidation temperature, pH, time and temperature of aging, and time and temperature of the heat treatment of the sample [13, 14].

Today nanodispersed aluminum is produced by electric explosion process in nitrogen, carbon dioxide, and their mixtures, with nitrogen, argon, air, and carbon dioxide as passivating media [15]. In this study we examined how the media used for explosion and passivation affect the activity of nanodispersed aluminum in reactions with water and the composition of the oxidation products.

EXPERIMENTAL

In the study we used samples of nanodispersed aluminum powder (NDP) prepared by electric explosion of aluminum wire in argon, nitrogen, carbon dioxide, and their mixtures and passivated with nitrogen, air, and carbon dioxide (Table 1). We used the following notation: medium in which the wire was exploded–slash–gas used for powder passivation.

The kinetics of the oxidation of nanodispersed aluminum with water were studied with a gasometric unit provided with software for measuring the gas volume [16]. The cell with distilled water was ther-
mostated at 60°C to completely remove gases dissolved in water, after which nanodispersed aluminum was added, and the volume of the released hydrogen was measured. From the kinetic curves we determined the maximal and mean rate of hydrogen evolution. We also calculated the conversion $\alpha$ as the ratio of the hydrogen volume actually released during the reaction to the theoretically expected volume.

The active metal content of aluminum samples was evaluated volumetrically from the hydrogen evolution in oxidation of nanodispersed aluminum with a NaOH solution [17].

Aluminum oxyhydroxides (AOHs) were prepared by the procedure described in [13]. Aluminum powders were thermostated in water (salt content 50 g l$^{-1}$, 55°C) with vigorous stirring of the suspension. Then the AOH powders were filtered off, washed with distilled water to neutral reaction, and dried.

The specific surface area $S_p$, pore volume, pore size, and distribution of mesopore volume with respect to size were determined by thermal desorption of nitrogen on a Sorbomter-M surface area analyser (Katakong Private Company, Novosibirsk). The landing area of the adsorbate gas was taken equal to 0.162 nm$^2$ [18].

The content of structural water in AOHs was calculated from the results of derivatographic studies performed with a Q-1500 D derivatograph in the dynamic mode (heating rate 10 deg min$^{-1}$) in the range 20–1000°C in air. The phase composition of AOHs was determined from the diffraction patterns taken with a DRON-3 diffractometer in the range of medium and large angles ($2\theta$ = 3°–60°, CuK$_\alpha$ radiation) with continuous scanning at a rate of 1 deg min$^{-1}$.

The morphology of nanodispersed aluminum particles and aluminum oxyhydroxides was studied with transmission electron microscopy (TEM, 125 kV). A suspension of a powder in ethanol was applied onto an object-plate and dried. A carbon layer was sputtered in a vacuum onto the object-plate with the sample. The extract carbon replica was separated with an aqueous solution of gelatin. After dissolving gelatin, the carbon replica with the powder was placed on a copper grid. To determine the mean size of powder particles and their size distribution, 300–500 particles were measured.

The maximum of the size distribution of aluminum nanoparticles is at 30–55 nm, with the smallest particles formed in CO$_2$ (Table 1). The electron micrograph and histogram of particle distribution of one of the samples prepared in N$_2$/CO$_2$ are shown in Fig. 1. Aluminum nanoparticles prepared in Ar and passivated with air (Ar/air) contain 80%, and the N$_2$/N$_2$ and N$_2$/air samples, about 75% active aluminum. Introduction of CO$_2$ into the explosion chamber leads to aluminum oxidation. The active aluminum content decreases to 16% on complete replacement of N$_2$ by CO$_2$. Simultaneously, the specific surface area of the samples increases with increasing concentration of CO$_2$. A considerable increase in the specific surface area of aluminum nanopowders prepared by electric explosion may be due both to formation of smaller particles and to formation on their surface of oxides having a larger surface area than aluminum metal (Table 1).

All the aluminum NDPs studied are oxidized with water in one step (Fig. 2). The initial oxidation rate