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Original Research

Chemical behaviour of Al/Cu nanoparticles in water

N.V. Svarovskaya[a,b,c], A.V. Berenda[b], O.V. Bakina[a,c,*], E.A. Glazkova[a,c], A.S. Lozhkomoev[a,c], E.G. Khorobraya[a], V.V. Domashenko[a], M.I. Lerner[a,c], A.N. Fomenko[a,c]

[a]Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences (ISPMS SB RAS), 2/4, pr. Akademichesky ave., Tomsk 634021, Russia

[b]National Research Tomsk State University (TSU), 36 Lenina ave., 634050 Tomsk, Russia

[c]National Research Tomsk Polytechnic University (TPU), 30 Lenina ave., 634050 Tomsk, Russia

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Abstract

Bimetallic Al/Cu nanoparticles with Al/Cu composition 10:90, 20:80, 40:60 were produced by method of simultaneous electrical explosion of metal pairs in the argon atmosphere. Nanopowders containing 20% and 40% (mass) of aluminum interacted with water at 40–70 °C and formed composite particles that were porous structures of nanopetal pseudoboehmite with nanosized copper-containing inclusions inside. Aluminum in nanopowder with Al/Cu composition 10:90 did not react with water, as far as it is in the phase of intermetallic compounds $CuAl_2$ and Cu_4Al_9. Nanocomposite produced can be used as an active component of antibacterial agents.

Keywords: Nanopowders; Bimetallic nanoparticles; Composite nanoparticles

1. Introduction

Emergence of resistant microorganism strains added extra relevance to the development of new antimicrobials capable of becoming an alternative to conventional antibiotic and antiseptic agents [1,2]. As a result there is renewed interest in biocidal metals (silver, zinc, copper) [3–5]. Use of metal nanoparticles as antibacterial agents is a promising field [6]. Developed surface of nanopowders allows considerably reducing, often by an order of magnitude, the metal concentration without undermining antibacterial effect [7]. On the other hand, metallic nanoparticles ensure prolonged migration of small concentrations of metal into the medium [8]. This makes them less toxic compared to soluble metal compounds and more active compared to massive metal [9]. Copper, thanks to its low cost, is an attractive antibacterial additive for medical use items and single-use medical wear, which encourages research into antibacterial activity of copper nanoparticles [10–13].

Composites containing adsorbent and antimicrobial agent at the level of one particle are a new generation of materials with considerable potential in the field of biomedicine [14,15].

Copper nanoparticles exert their impact upon microbial cells during direct contact [16]. In order to increase the number of contact points, one can unite copper particles with a substance manifesting membrane-acting properties, for instance, with a microbiologically active sorbent [17,18]. Electropositive nanopetal pseudoboehmite is such a sorbent; it forms during interaction of aluminum nanoparticles or aluminum nitride with water [19]. One can expect that composite nanoparticles with structure uniting pseudoboehmite nanopetals and nanosized copper particles will possess higher antimicrobial activity compared to copper nanoparticles. Nanocomposite produced can be used as an antibacterial agent when creating medical use materials.

The present paper describes simple synthesis of new composite nanoparticles that are nanosized copper-containing particles surrounded by pseudoboehmite nanopetals. Bimetallic Al/Cu nanoparticles produced from copper and aluminum

*Corresponding author at: Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences (ISPMS SB RAS), 2/4, pr. Akademicheskii, Tomsk 634021, Russia.
Tel.: +7 3822 49 18 81; fax: +7 3822 49 25 76.
E-mail addresses: aov862@sibmail.com, ovbakina@ispms.tsc.ru (O.V. Bakina).
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by method of electric explosion of wires (EEW) in the argon atmosphere were used as precursors.

2. Material and experimental methods

2.1. Precursor synthesis

Nanopowders of Al/Cu bimetallic particles were produced by the method of simultaneous electric explosion of aluminum and copper twisted wires in the atmosphere of argon. Conceptual scheme of nanopowder production (Fig. 1) is as follows: two twisted wires (Al and Cu) are subjected to high-density current pulse ($\sim 10^7$ A/cm^2) released during capacitor bank discharge. Pulse goes through the wires, and explosive destruction of metals is observed; it is accompanied by bright flash, blast wave, metal dispersion and fast expansion of explosion products into surrounding gas. Explosion products are cooled down and form nanoparticles. Nanopowders are pyrophoric immediately after synthesis; that is why they are passivated by slow letting-to-air method before use. Mass ratio of aluminum (w_{Al}) and copper (w_{Cu}) in nanopowder samples was regulated by conductor diameters (d_{Cu} and d_{Al}) (Table 1). Calculation data conform well to the results of composite particle analysis by the EDAX–TEM method.

2.1.1. Synthesis of Al/Cu oxidation products

Particles were obtained by oxidation of nanopowders with water relying on the following methodology. 0.5000 ± 0.0001 g of nanopowder were put into the thermally insulated reaction vessel, 50 ml of distilled (reverse osmotic) water were added, the mix was heated to 60 °C and constantly stirred. The course of reaction was controlled on the basis of hydrogen release volume that was measured every 10 s. Kinetic curves of sample interaction with water were constructed in coordinates V (ml/s g)$-t$ (min), where V is the volume of hydrogen (ml) released during interaction of active aluminum with mass, m (g), in the sample composition over the time period t (s). Mass of active aluminum in samples was measured by volumetric method before that [20].

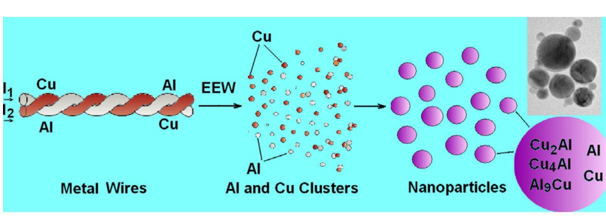

Fig. 1. Conceptual synthesis scheme of Al/Cu nanoparticles.

Table 1
Mass ratio of Al and Cu in nanopowder samples.

Sample	d_{Cu} (mm)	d_{Al} (mm)	w_{Cu} (%)		w_{Al} (%)		
			Est.	EDAX-TEM	*Est.*	EDAX–TEM	*Volum.*
1	0.25	0.16	90	89	10	11	0
2	0.30	0.25	80	79	20	20	5
3	0.25	0.35	60	60	40	37	23
4	–	0.30	–	–	–	–	90

2.2. Physical and chemical properties of nanopowders

Morphology and size of nanoparticles and their agglomerates were identified by method of transmission electron microscopy (JEOL 2000FX, JEM, Japan, at accelerating voltage 150 kV). Average size of nanoparticle agglomerates was estimated by the sedimentation method (disk centrifuge CPS DC 24,000, CPS Instrument, USA). Experimental data were processed using original software Disc Centrifuge Control System (DCCS).

Phase composition was determined using X-ray diffraction method on CuK$_\alpha$ radiation, $\lambda = 1.54056$ Å (XRD-6000, Shimadzu, Japan). Phases were identified using software complex PCPDFWIN. Texture characteristics were determined using Sorbtometer M (Katakon, Russia) based on low-temperature nitrogen adsorption. Specific surface was calculated by 5-point BET method.

The antimicrobial activity of the samples of composite particles was determined by radial diffusion in agar [21] using bacteria *Escherichia coli* K-12 (Russian National Collection of Industrial Microorganisms). A 0.5 McFarland (1×10^7–1×10^8 CFU/mL) concentration of bacterial suspension was uniformly inoculated on Nutrient agar (NA) solidified in 90 mm Petri dishes. Holes in the plates were made with stainless steel cylinders ($D = 10$ mm) and the samples of concentration 100 mg/L were added. The dishes were incubated at a constant temperature incubator at 37 °C for 24 h. The inhibition zone (IZ) diameter was measured and recorded a vernier caliper. All the measurements were performed in triplicate and the results were expressed as mean ± standard deviation.

3. Results and discussion

3.1. Al/Cu synthesis

In case of simultaneous electric explosion of aluminum and copper wires in the argon atmosphere the spherical 80–120 nm particles formed regardless of the wire diameter ratio.

According to the previous research [21], during the electric explosion of monometallic wire the first dispergation of metal to the liquid clusters having a few nanometers size takes place. Then liquid clusters are combined together to form nanoparticles. Probably a similar process occurs when two wires of aluminum and copper are dispersed. During the electric explosion of two conductors the clusters of aluminum and copper are formed, and then they collide with each other and are combined into nanoparticles.

According to EDAX–TEM analysis data, aluminum and copper were uniformly distributed over the volume of particles, as shown in Fig. 2. The surface of particles is covered by thin passivating film, most likely oxide. Oxygen content in particles was around 5%. Nitrogen content in particles was less