

Original Research

Chemical behaviour of Al/Cu nanoparticles in water

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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 CuAl₂ and Cu₄Al₉. Nanocomposite produced can be used as an active component of antibacterial agents.

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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 anti-septic 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

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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/cm²) 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].

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 $\text{CuK}\alpha$ radiation, $\lambda = 1.54056$ Å (XRD-6000, Shimadzu, Japan). Phases were identified using software complex PCPDFWIN. Texture characteristics were determined using Sorbtometer M (Katakona, 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 $\pm$ 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

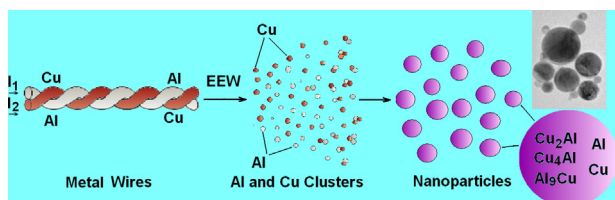


Fig. 1. Conceptual synthesis scheme of Al/Cu nanoparticles.

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

Sample	d_{Cu} (mm)	d_{Al} (mm)	w_{Cu} (%)		w_{Al} (%)		Volum.
			Est.	EDAX-TEM	Est.	EDAX-TEM	
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

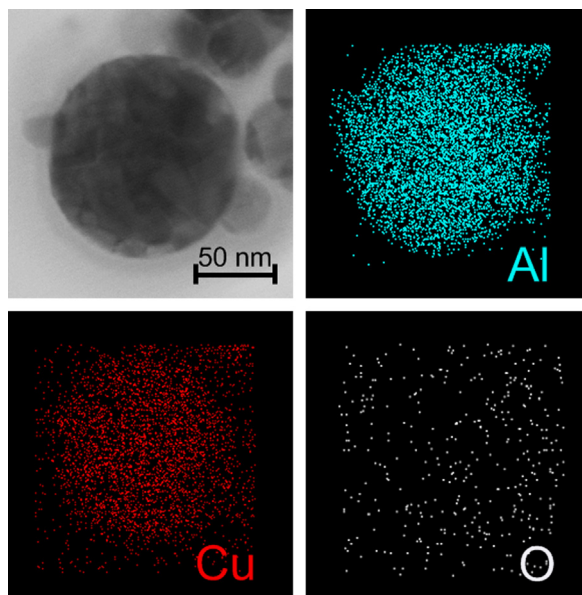


Fig. 2. TEM image of Al/Cu particle and distribution of elements over the particle.

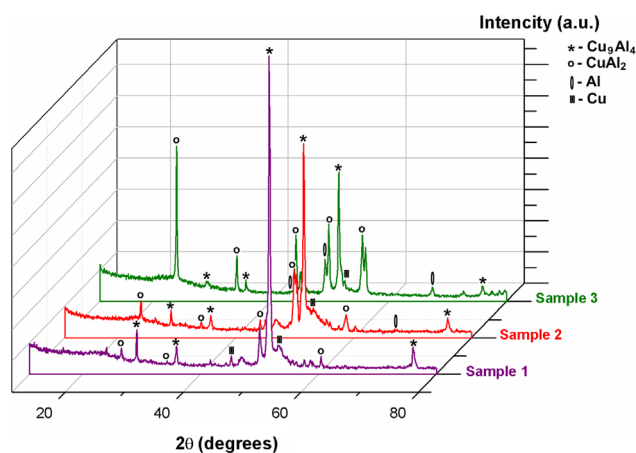


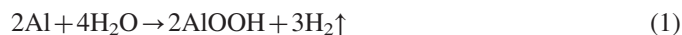
Fig. 3. XRD spectra of Al/Cu samples.

than 0.05%; that is why nitride or oxynitride nature of the passivating film is unlikely. On diffractograms of all nanopowder samples the main reflexes correspond to intermetallic Cu_9Al_4 compounds. The samples also contain phases of metallic Al, Cu, as well as CuAl_2 solid solution (Fig. 3), which corresponds to the diagram of Cu–Al system state [23]. For sample 1 containing 10% of aluminum the phase of metallic aluminum was not found. Comparison of EDAX–TEM and X-ray phase analysis data suggests that the particles have complex internal structure and consist of clusters with different phase composition. Activity of metallic aluminum in reaction with water will be determined by position of aluminum clusters in the particle and their availability for water.

3.2. Oxidation of Al/Cu nanopowders

Aluminum in the composition of samples 2 and 3 is chemically active and interacts with water already at 60 °C,

just as sample 4 (aluminum nanopowder). Reaction is exothermic and is accompanied by hydrogen release according to Eq. (1).



Gas release was not observed for sample 1 (Al/Cu 10:90), as far as practically all aluminum in it is bound in intermetallic compounds that do not react with water under experiment conditions.

It can be observed that the gas release kinetic curves of samples 2 (Al/Cu 20:80) and 3 (Al/Cu 40:60) have a more complex shape compared to gas release curve of sample 4 – aluminum nanopowder (Fig. 4). And the induction period during which there is no gas release is reduced considerably, but one can observe hydration and dissolution of surface oxide film. Induction period has practically no dependence on the powder composition.

Three maximum points can be observed on kinetic gas release curves of samples 2 and 3. It is likely to be due to the non-uniform structure of composite nanoparticles, where grains of aluminum phase are located randomly between phases of intermetallic compounds and copper and have different availability for water. As the reaction deepens and the structure of initial particle is destroyed, aluminum from the particle internal volume becomes available. Oxidation of aluminum with water in the presence of iron and especially copper admixtures occurs following the mechanism of electrochemical corrosion [24]. The rate of corrosion increases with the increase in copper content of samples due to increase in the number of aluminum–copper contact points and relative decrease in aluminum area (anode) in relationship to copper area (cathode).

3.3. Characteristics of Al/Cu oxidation products

Specific surface, phase composition and particle morphology of sample 1 (Al/Cu 10:90) did not change after heating in water, which is in agreement with the absence of reaction indicators observed.

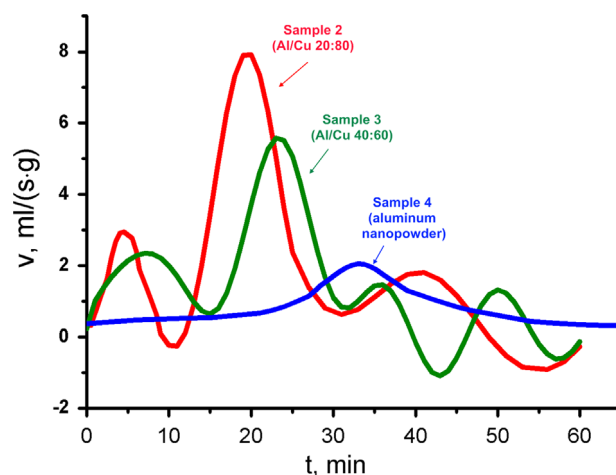


Fig. 4. Gas release curves: of Al/Cu samples and aluminum nanopowder.

Composite particles with sizes less than 1.0 μm produced after oxidation of samples 2 (Al/Cu 20:80) and 3 (Al/Cu 40:60) under experiment conditions are of special interest. They are structurally non-uniform electron-dense spherical inclusions surrounded with nanopetals (Fig. 4). In terms of size (100–300 nm wide and 5–7 nm thick) nanopetals are analogous to oxidation products of electroexplosive Al and Al/AlN nanopowders under the same conditions [25]. Examination of substructural characteristics of agglomerates by comparing bright-field and dark-field TEM images (Fig. 5) and element composition of agglomerates by energy dispersive analysis (Fig. 6) allowed establishing that electron-dense inclusions are enriched with copper and consist of blocks with size less than 10 nm.

According to X-ray phase analysis data, porous particles obtained contain poorly crystallized pseudoboehmite – the product of metallic aluminum transformation (Fig. 7). Moreover, in all of them metallic copper and intermetallic compounds were found in the same ratios as in initial nanopowders. This allows suggesting that copper and intermetallic compound phases in the initial Al/Cu nanoparticles are in the form of inclusions with size less than 10 nm and are in contact with aluminum phase inclusions located between them. When aluminum reacts with water and porous products are formed, the composite particle grows in size, and copper-containing inclusions shift, but retain the size, shape and relatively uniform distribution over the particle volume. Specific surface of the products of sample 2 reacted with water was 31 m^2/g , of sample 3 – 130 m^2/g . This was due to the fact that sample 3 contains more metallic Al and hence forms larger number of porous transformation products.

The synthesized composite nanoparticles had antimicrobial activity towards *E. coli*. The inhibition zone (IZ) of products of oxidation of samples 1, 2, 3 was 5.1 ± 0.1 , 8.4 ± 0.5 and 8.4 ± 0.2 , respectively. The product of oxidation of sample 4 had not the antimicrobial activity, and IZ was 0 mm after 48 h of exposure.

4. Conclusion

The method of simultaneous electric explosion of copper and aluminum wires in the argon atmosphere was used to

produce powders consisting of bimetallic Al/Cu nanoparticles in ratios 10:90, 20:80 and 40:60. Phase composition of nanoparticles is represented by phases of copper, aluminum

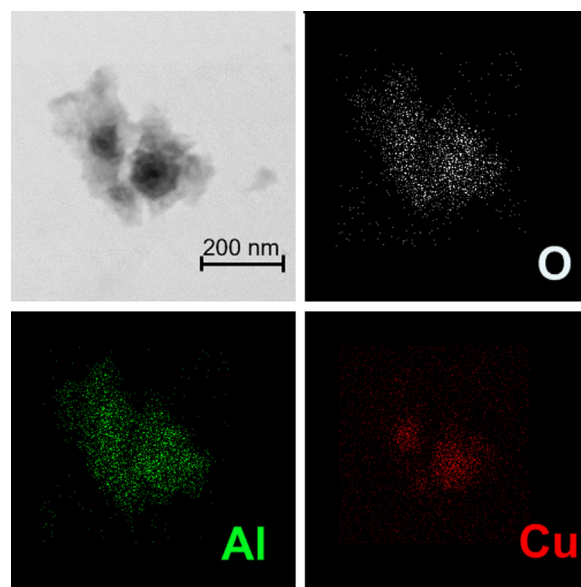


Fig. 6. TEM image of Al/Cu particle and distribution of elements over the particle.

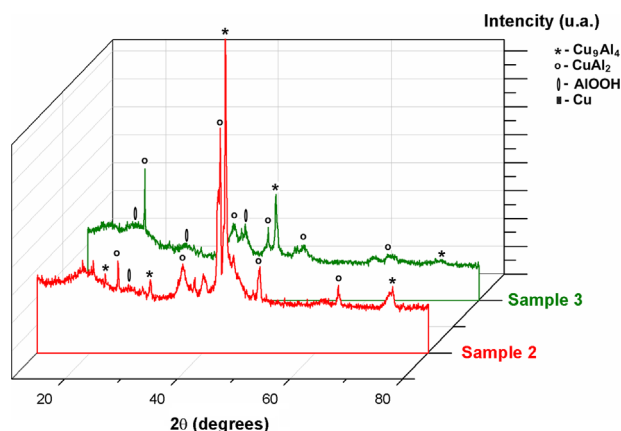


Fig. 7. XRD spectra of products of Al/Cu samples interaction with water.

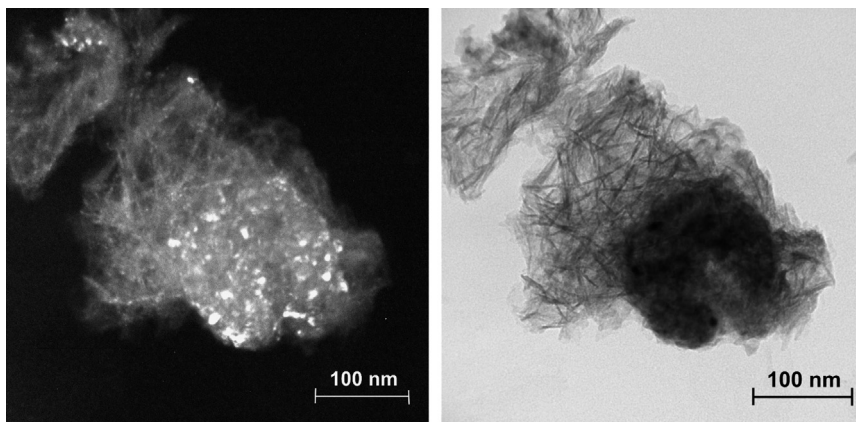


Fig. 5. TEM images of Al/Cu oxidation products.

and intermetallic compounds Cu_2Al , Cu_4Al , Al_9Cu , and phase ratio is determined by the ratio of metals in nanoparticles. Chemical behavior of nanopowders in water at 60 °C has been studied and demonstrated that induction period in these powders is smaller and reaction rate is higher than in case of aluminum nanopowder with comparable particle size. This is due to electrochemical mechanism of aluminum corrosion in the presence of copper. The increase in mass share of copper in nanoparticles from 60% to 80% (mass) leads to acceleration of reaction due to increase in aluminum/copper contact areas and increase in copper surface compared to aluminum. In case of further increase of copper share in nanoparticles to 90% practically all aluminum is bound into intermetallic compounds and does not react with copper and water. The products of nanopowder interaction with water are composite nanoparticles that are porous structures of nanopetal pseudoboehmite with copper-containing inclusions inside. The composite nanoparticles exhibit the highest antimicrobial activity.

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