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Characterization of copper and aluminum AC electrochemical oxidation products

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Abstract

Non-equilibrium electrochemical metal oxidation is one of the methods to obtain the power-saturated nanosized metal oxides. AC electrochemical separate copper and aluminum oxidation in an aqueous sodium chloride solution is performed. It results in the phase transformations of the obtained copper (I) oxide and boehmite during the storing in solution. Phase composition, pore structure characteristics and morphology of the products are considered. Their pore structure is preferably formed by mesopores. Carbonate ion adsorption of metal oxides/oxyhydroxides is due to their high affinity. The contamination of the power-saturated nanosized products of electrolysis with carbon-containing impurities is not a problem because some undesirable compounds may be removed by heat treatment, but others do not negatively affect the operating performance. Product of AC electrochemical copper oxidation is characterized by particle shape anisotropy (spindle-shaped particles of copper oxide and copper carbonate hydroxide wire bundles) that positively affects the some properties. The product of AC electrochemical aluminum oxidation has a flower-like structure.

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1. Introduction

Metal oxides constitute the largest share of powdered nanomaterials. There are a set of methods to obtain

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functional metal oxide materials. Among them the non-equilibrium syntheses can be emphasized: Merzhanov et al.¹ discovered the self-propagating high-temperature synthesis (SHS) of different types of materials, Zyryanov² described mechanochemical synthesis of mixed oxides, Korobochkin³ developed the processes of nanodispersed oxide obtaining by electrochemical metal oxidation under alternating current.

Metal AC polarization is the most appropriate method for the nano-powder synthesis of metal oxides which are used in catalytic and sorption processes. It was determined that the non-equilibrium electrochemical oxidation the number of metals produces metal oxides with the pore structure characteristics exceeded ones of industrial products several times.

Copper and aluminum oxides are essential compounds for an active developing petrochemical industry. Thus, the materials based on these compounds attract the scientist attention and are widely produced either separately^{4,5} or in the form of binary system⁶⁻¹².

This work focuses on the characterization of copper and aluminum AC electrochemical separate oxidation products. The characterization of copper and aluminum AC electrochemical simultaneous oxidation products of will be published afterwards.

2. Experimental

Electrochemical metal oxidation by industrial frequency alternating current has been realized according to the method described in³.

The synthetic procedure was as follows: electrochemical metal oxidation was carried out in aqueous sodium chloride solution with concentration of 3 wt % at the temperature of 90 °C and current density of 1 A/cm². The plates of copper (mark M1) and aluminum (mark A0) were used as soluble electrodes.

Electrolysis products were washed with distilled water and air-dried at the temperature of 110 °C for 3 hours. The oven was naturally cooled to room temperature when the drying time was finished.

X-ray diffraction (XRD) measurements were performed using DRON-3M diffractometer with CuK α radiation ($\lambda=1.5418 \text{ \AA}$) at 25 mA and 35 kV. The data were collected from 10 to 70° at a counting rate of 40/min. The PDF 2 database was used to identify the phase composition.

The surface area of the particle was determined from the nitrogen adsorption-desorption isotherms (Brunauer-Emmett-Teller method) at 77 K with NOVA 2200-e surface analyzer. The cross-section of the nitrogen molecule was assumed to be 0.162 nm². Total pore volume was calculated at relative N₂ pressure (P/P₀) of 0.999.

Scanning electron microscopy (SEM) analysis was carried out on JEOL JSM-7500FA at 20 kV to evaluate surface morphology of the samples. Element concentration was measured by the energy dispersive X-ray spectroscopy (EDS).

Nomenclature

A	mass element percentage in AC electrochemical metal oxidation product (ms %)
B	mol element percentage in AC electrochemical metal oxidation product (mol %)

3. Results and discussion

The electrochemical copper oxidation in a neutral medium leads to the formation of cupreous oxide (Cu₂O) as opposed to the oxidation in the alkaline medium when cupric oxide (CuO) is formed. Cupreous oxide is oxidized to cupric oxide at the aging in solution¹². The product of non-equilibrium electrochemical oxidation of aluminum is aluminum oxyhydroxide (boehmite, AlOOH).

Interaction of copper (I) oxide with air carbon dioxide leads to the formation of copper carbonate hydroxide (malachite) Cu₂(OH)₂CO₃. Aluminum oxyhydroxide is characterized by cation absorption and carbonate ion adsorption. It results in the formation of sodium aluminium carbonate hydroxide NaAl(CO₃)(OH)₂. Several absorption bands on IR spectra indicate reliably the formation of this compound¹². Since this compound is an

impurity, its influence on the properties of the electrolysis product may be neglected. Carbonate ion adsorption on the surface of some metal oxyhydroxides is due to their high affinity.

Pore structure parameters (total pore volume, specific surface area) of the AC electrochemical metal oxidation products are considerably different (fig. 1). It arises from the metal nature, consequently, the tendency of metal oxide to coagulation, recondensation and coalescence.

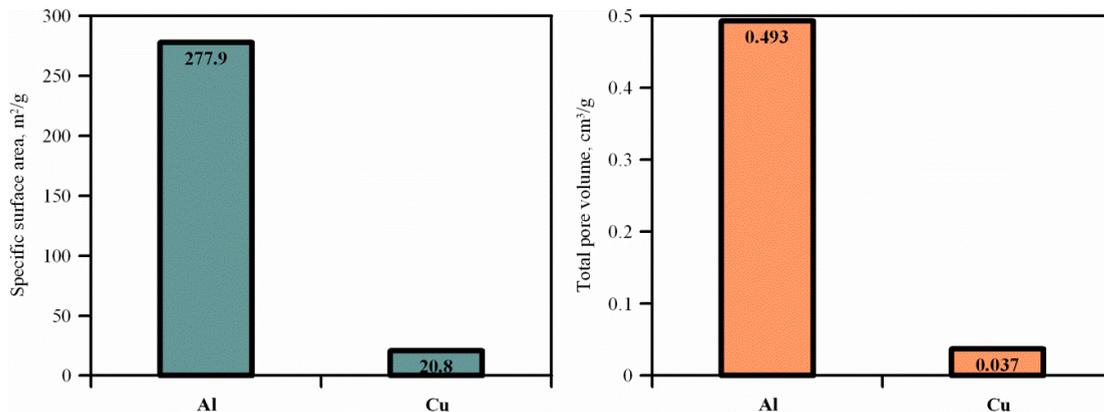


Fig. 1. Pore size and total pore volume distributions of the AC electrochemical copper and aluminum oxidation products

Hysteresis loops of N₂ adsorption-desorption isotherms indicate the existence a certain amount of mesopores in the porous structure of the copper and aluminum AC electrochemical oxidation products (fig. 2, 3, insets)¹³. It is difficult to see the hysteresis loop in the inset of fig. 2, but the pore size and surface area distributions clearly show not only the mesopore presence, but their predominance in the pore structure of the electrochemical copper oxidation product.

The specific surface area is generally formed by the surface of mesopores with the sizes near the lower limit of the range: up to 10 nm in the cross-section for the copper oxidation product (fig. 2) and 3.8–4.3 nm in the cross-section for the product of aluminum oxidation (fig. 3).

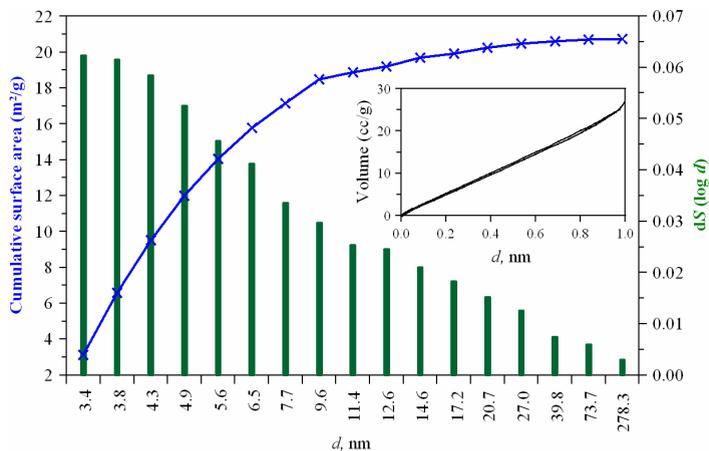


Fig. 2. Surface area distribution and nitrogen adsorption-desorption isotherm (inset) of the AC electrochemical copper oxidation product

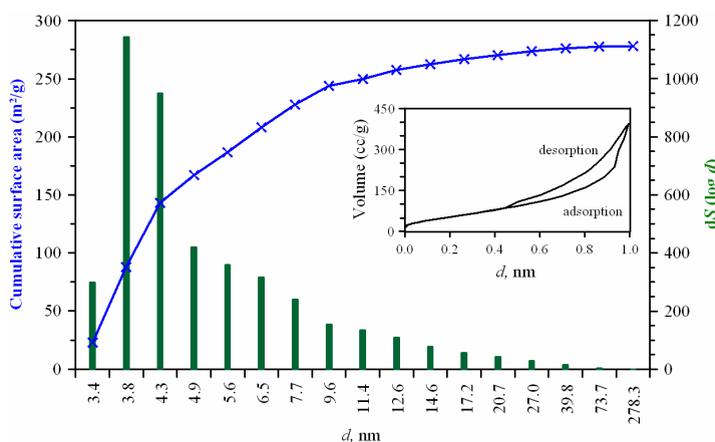


Fig. 3. Surface area distribution and nitrogen adsorption-desorption isotherm (inset) of the AC electrochemical aluminum oxidation product

According to the SEM images, spindle-shaped particles of copper oxide coexist with bundles of copper carbonate hydroxide wires (fig. 4, a). For spindles the lengthwise and cross dimensions are 1–3 μm and 0.5–1.0 μm , respectively. The lengthwise and cross dimensions of wire bundles are 4–6 μm and 2.5–3.0 μm , respectively. Misra et al.⁵ showed the influence of the shape of CuO particles on the suspension stability and particle dissolution. The suspension of spindle-shaped CuO particles has the least stability. It is due to the lowest point of zero charge (PZC) of spindles, consequently, the closest PZC to the medium pH in comparison with the particles of other shapes. The PZC dependence on a particle shape is believed to be a result of the different adsorption and affinity of protons on the surfaces which areas and energies are considerably different. The lowest suspension stability and surface area of the spindle-shaped CuO particles lead to the slowest dissolution and the least quantity of Cu released.

The AC electrochemical aluminum oxidation product has a flower-like structure (up to 5 μm diameter) that consist of two-dimensional nanosheets (~ 10 nm thick) (fig. 5, a)⁴.

EDS spectra (fig. 4, 5, b) were obtained at the points inside the areas indicated in fig. 4, 5, a. Quantitative results of EDS analysis are listed in tables 1 and 2.

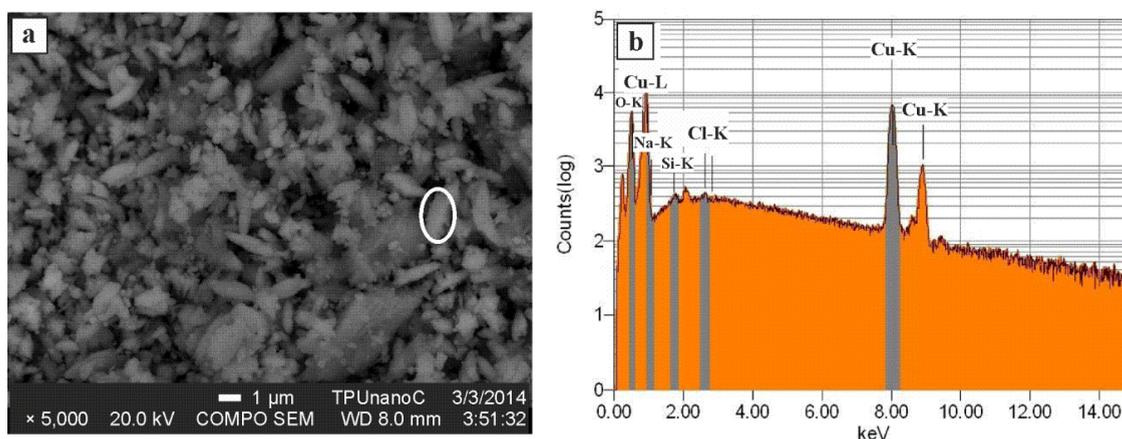


Fig. 4. SEM-EDS image of AC electrochemical copper oxidation product (magnification of 5,000)

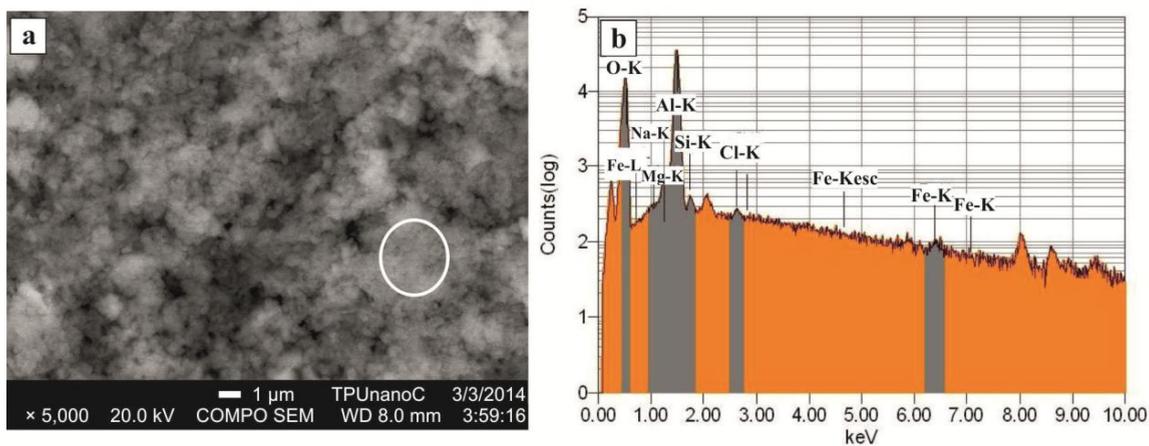


Fig. 5. SEM-EDS image of AC electrochemical aluminum oxidation product (magnification of 5,000)

Table 1. Quantitative results of EDS analysis of the product of AC electrochemical copper oxidation

Elements	Column A (m _s)	Column B (m _{mol})
O	15.46	39.68
Cu	79.43	51.32
Na*	4.88	8.72
Cl*	0.14	0.17

Table 2. Quantitative results of EDS analysis of the product of AC electrochemical aluminium oxidation

Elements	Column A (m _s)	Column B (m _{mol})
O	47.85	60.78
Al	51.84	39.05
Na*	0.04	0.03
Cl*	0.13	0.07

Despite the formation of carbon-containing compound¹⁴ it is impossible to detect reliably the carbon in the samples because it is used as a substrate at EDS analysis. The product of electrolysis is powder. Hence, there are some areas of a substrate surface where the layer of sample is not continuous. Therefore, the characteristic radiations of both carbon substrate and carbon containing in the sample cannot be divided.

Metal electrochemical oxidation has been carried out in a sodium chloride solution. Na- and Cl-traces in the composition of the electrolysis product grow from the interaction of electrolyte ions with the product of electrolysis.

4. Conclusion

AC electrochemical oxidation of copper and aluminum in a sodium chloride solution is an effective way for the nanostructured oxide synthesis. Both copper- and aluminium-containing samples are characterized by mesopore structures that are composed of 1- and 2-dimensional nanosized particles. The contamination of the power-saturated nanosized products of electrolysis with impurities is not a problem because some undesirable compounds may be removed by heat treatment, but others do not negatively affect the operating performance.

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