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Evolution of Nanostructured Materials Produced by Separate Electrochemical Oxidation of Copper and Aluminum

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Abstract. This paper covers the results of the composition and structure evolution of nanostructured materials produced by separate electrochemical oxidation of metals (copper and aluminum). The electrolysis products after short-term and long-term aging were characterized by XRD (X-ray diffraction) and DSC (differential scanning calorimetry) analysis. There is the difference in aging of nanostructures of copper- and aluminum-compounds. Short-term aging results in the phase transformation of copper (I) oxide and the stability of aluminum oxyhydroxide (boehmite). Copper (I) oxide is oxidized to copper (II) oxide and copper carbonate hydroxide. At long-term aging the oxidation of copper (I) oxide does not completed because the Pilling–Bedworth ratio for copper (II) oxide, copper carbonate hydroxide is greater than one. The structure of all copper-containing compounds (copper (I) oxide, copper (II) oxide, copper carbonate hydroxide) is changed. It results in the increases of both the interplanar spacing and the temperature of the phase transformations. Coherent scattering region (CSR) of boehmite and copper (I) oxide are 3–4 nm and 20–30 nm, respectively, and does not change at short-term and long-term aging.

Keywords: electrolysis, nanomaterials, phase composition, aging.

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Эволюция наноструктурированных продуктов индивидуального электрохимического окисления меди и алюминия

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Аннотация. В работе представлены результаты исследования эволюции состава и структуры наноструктурированных материалов, полученных при раздельном электрохимическом окислении металлов (медь и алюминий). Продукты электролиза после кратковременного и длительного старения охарактеризованы методами РФА (рентгенофазовый анализ) и ДСК (дифференциальная сканирующая калориметрия). Установлено различие в старении наноструктур соединений меди и алюминия. Кратковременное старение приводит к фазовому превращению оксида меди (I) и стабильности оксигидроксида алюминия (бемита). Оксид меди (I) окисляется до оксида меди (II) и основного карбоната меди. При длительном старении оксида меди (I) окисление происходит не полностью, так как отношения Пиллинга-Бедворта для оксида меди (II) и гидроксида карбоната меди больше единицы. Структура всех медьсодержащих соединений (оксид меди (I), оксид меди (II), гидроксид карбоната меди) изменяется. Это приводит к увеличению как межплоскостных расстояний, так и температуры фазовых превращений. Область когерентного рассеяния (ОКР) бемита и оксида меди (I) составляет 3–4 нм и 20–30 нм, соответственно, и не изменяется при кратковременном и длительном старении.

Ключевые слова: электролиз, наноматериалы, фазовый состав, старение.

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Introduction

An important part of powdered nanomaterials is metal oxides. A number of non-stationary methods are used to produce the functional metal oxide materials [1]. It is because the disordered structure and high storage of internal energy that determine the high reactivity to phase transformations of metal oxides and their use in various processes.

The use of alternating current to carry out the electrochemical metals oxidation results in nanostructured oxides and multicomponent nanostructured oxide materials [2].

There are a number of electrochemical methods to produce coatings of metal oxides [3], mixed oxides [4], layered double hydroxides [5] and perovskites [6].

It is known that nanomaterials are characterized by interaction with compounds contained in mother solution or in the environment. New phases are formed; they may be of interest not only for science, but also for practical application [7–9].

There are the different methods of analysis to characterize the nanostructures of oxides. The choice of method depends on what information is to be obtained. To evaluate the phase compositions and coherent scattering regions (CSR), X-ray diffraction (XRD) is used. The temperatures of phase and structure transformations are provided by analysis of differential scanning calorimetry and thermogravimetric analysis (DSC/TG) [10]. The specific properties of matter at the nanoscale level are the reason of the difference the methods that can be applied to carry out the thermal analysis both bulk and dispersed materials [11].

The purpose of this work is to study the influence aging on composition and properties of nanostructured powders produced by separate electrochemical oxidation of copper and aluminum.

Research methodologies

Electrochemical oxidation of metals was carried out in a 3 wt% sodium chloride solution at the densities of alternating current of 1 A/cm². Metal plates (copper or aluminum) were used as soluble electrodes.

X-ray diffraction (XRD) measurements were performed at 30 mA and 40 kV (a Shimadzu XRD 7000 diffractometer, CuK_α radiation, $\lambda=1.5418 \text{ \AA}$). The range of 2θ is from 10 to 70°, counting rate is 2 θ min⁻¹. The phase compositions were identified by PDF 2 database, the coherent scattering regions (CSR) were determined with the program “Powder Cell 2.4”.

SDT Q600 V20.9 Build 20 was used to carry out thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in air at a heating rate of 10 °C min⁻¹ in the temperature range from ambient to 1000 °C.

Results and discussion

Electrochemical copper oxidation

The rate of electrochemical copper oxidation is 0.04 g/(cm²·h). Phase composition of nanostructured powder of copper (I) oxide was detected by XRD analysis. At the aging the copper (I) oxide is oxidized to copper (II) oxide, and the copper carbonate hydroxide (Cu₂(OH)₂CO₃) is formed [12].

Short-term aging (30 and 45 days) leads to an increase in the background line of XRD patterns due to amorphization of the structure during the formation of new phases. The result of the long-term aging (5 years) is the change of the structure (crystallization of the amorphous phase), because of this the background of XRD patterns becomes smoother and intensity of some Cu₂(OH)₂CO₃ peaks are increased (Fig. 1).

After aging for 60 days (Fig. 1, short-term aging), there is a small amount of Cu₂O in sample. According to the XRD results, the residual Cu₂O is not completely oxidized to CuO at long-term aging. This may be due to the fact that Cu₂O is located in the centers of particles coated with CuO that prevents oxygen access to Cu₂O.

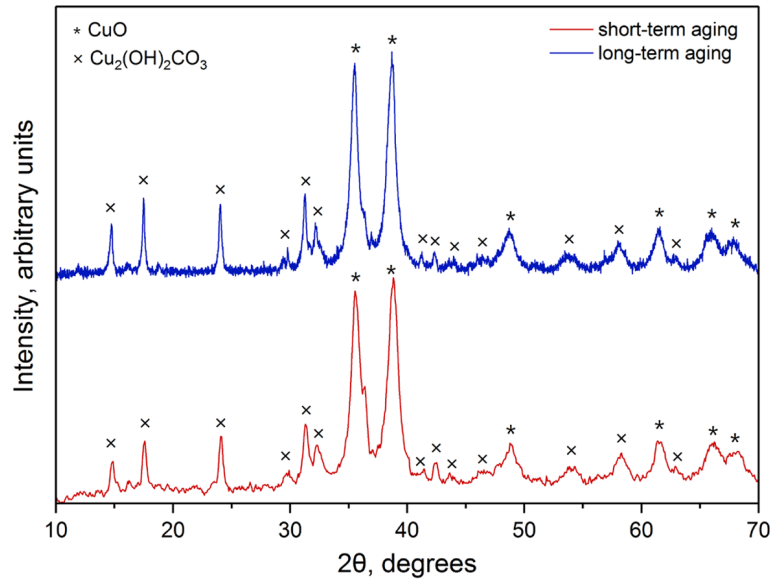


Fig. 1. XRD patterns of the nanostructured powders produced by electrochemical oxidation of copper

The protective effect of oxidation products depends on their structure, which is determined by the ratio of the volumes of oxidized and formed compounds (Pilling–Bedwards ratio / P–B ratio) [13], as well as the structure of oxidation products.

In this paper the Pilling – Bedwards ratio is determined by the following formulas:

$$\alpha_{\text{CuO}/\text{Cu}_2\text{O}} = \frac{V_{\text{CuO}}}{V_{\text{Cu}_2\text{O}}} = \frac{M_{\text{CuO}}/\rho_{\text{CuO}}}{n \cdot M_{\text{Cu}_2\text{O}}/\rho_{\text{Cu}_2\text{O}}} = \frac{M_{\text{CuO}} \cdot \rho_{\text{Cu}_2\text{O}}}{n \cdot M_{\text{Cu}_2\text{O}} \cdot \rho_{\text{CuO}}},$$

$$\alpha_{\text{Cu}_2(\text{OH})_2\text{CO}_3/\text{Cu}_2\text{O}} = \frac{V_{\text{Cu}_2(\text{OH})_2\text{CO}_3}}{V_{\text{Cu}_2\text{O}}} = \frac{M_{\text{Cu}_2(\text{OH})_2\text{CO}_3} \cdot \rho_{\text{Cu}_2\text{O}}}{n \cdot M_{\text{Cu}_2\text{O}} \cdot \rho_{\text{Cu}_2(\text{OH})_2\text{CO}_3}},$$

$$\alpha_{\text{Cu}_2(\text{OH})_2\text{CO}_3/\text{CuO}} = \frac{V_{\text{Cu}_2(\text{OH})_2\text{CO}_3}}{V_{\text{CuO}}} = \frac{M_{\text{Cu}_2(\text{OH})_2\text{CO}_3} \cdot \rho_{\text{CuO}}}{n \cdot M_{\text{CuO}} \cdot \rho_{\text{Cu}_2(\text{OH})_2\text{CO}_3}},$$

where M_{CuO} , $M_{\text{Cu}_2\text{O}}$, $M_{\text{Cu}_2(\text{OH})_2\text{CO}_3}$ – molar mass of CuO, Cu₂O and Cu₂(OH)₂CO₃ respectively, g/mol; ρ_{CuO} , $\rho_{\text{Cu}_2\text{O}}$, $\rho_{\text{Cu}_2(\text{OH})_2\text{CO}_3}$ – density of CuO, Cu₂O and Cu₂(OH)₂CO₃ respectively, g/cm³; ($\rho_{\text{Cu}_2\text{O}} = 6.11$ g/cm³, $\rho_{\text{CuO}} = 6.45$ g/cm³, $\rho_{\text{Cu}_2(\text{OH})_2\text{CO}_3} = 4.00$ g/cm³ [14]); n – number of atoms of the copper compound per 1 molecule of the aging product.

If the Pilling–Bedworth ratio is in the range from 1 to 2, the coating is passivating and provides a protecting effect against further surface oxidation [13]. The Pilling–Bedworth ratio is greater than one for copper compounds ($\alpha_{\text{CuO}/\text{Cu}_2\text{O}} = 1.05$, $\alpha_{\text{Cu}_2(\text{OH})_2\text{CO}_3/\text{Cu}_2\text{O}} = 2.35$, $\alpha_{\text{Cu}_2(\text{OH})_2\text{CO}_3/\text{CuO}} = 2.24$). Hence, the volume of CuO or Cu₂(OH)₂CO₃ is larger than the volume of Cu₂O, and the oxidation products form a continuous layer on the surface of the initial oxide. At the same time, due to the small particle size, high porosity, and nonstoichiometry of the oxidation products, the oxidation process does not stop after the formation of a thin layer of oxidation products. A small amount of Cu₂O after long-term aging probably remains in the centers of the large particles covered by thick layer.

The *Scherrer* equation [1] was used to calculate the coherent scattering region (CSR):

$$d = \frac{k\lambda}{\beta \cos \Theta}$$

where k is the Scherrer constant; λ is the wave length of the X-ray beam used (1.5418 Å); β is the full width at half maximum (FWHM) of the peak; Θ is the Bragg angle.

At both short-term and long-term aging CSR of boehmite and copper (I) oxide are 3–4 nm and 20–30 nm, respectively [2].

There is a XRD peak shift of all copper-containing compounds (copper (I) oxide, copper (II) oxide and copper carbonate hydroxide $\text{Cu}_2(\text{OH})_2\text{CO}_3$) to the large values of the interplanar distance (Tables 1–3). The increase in interplanar distances is a result of the interaction of nanostructures with oxygen and CO_2 of the atmosphere.

The aging results in a temperature increase of the phase transformations (Fig. 2).

The increase of endothermic effects (peak *I*) of dehydration as the ageing result is due to structure ordering.

The small amount of Cu_2O cannot be identified by XRD analysis but it is detected by DSC measurements. At the temperature increase, Cu_2O is oxidized to CuO and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ is decomposed. In the temperature range of 150–280 °C, there is an overlap of the exoeffect from the oxidation of Cu_2O and the endoeffect from the first stage of decomposition of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (peak *II*). When Cu_2O is oxidized at long-term aging, the Cu_2O content decreases and the exoeffect is change in the same way.

Table 1. Interplanar spacing of copper (I) oxide

Sample	Interplanar spacing of copper (I) oxide, nm			
	(110)	(111)	(200)	(220)
PDF No. 05–0667	0.3020	0.2465	0.2135	0.1510
5 days	0.3017	0.2466	0.2135	0.1508
30 days	0.3017	0.2458	0.2131	0.1508
45 days	0.3024	0.2462	0.2131	0.1508
60 days	0.3029	0.2488	0.2134	0.1509
5 years	0.3040	0.2481	0.2136	0.1510

Table 2. Interplanar spacing of copper (II) oxide

Sample	Interplanar spacing of copper (II) oxide, nm			
	(111)	(–111)	(–202)	(–222)
PDF No. 05–0661	0.2524	0.2311	0.1867	0.1375
5 days	0.2523	0.2321	–	–
30 days	0.2523	0.2317	0.1866	0.1372
45 days	0.2525	0.2317	0.1866	0.1375
60 days	0.2525	0.2320	0.1868	0.1380
5 years	0.2527	0.2328	0.1870	0.1393

Table 3. Interplanar spacing of copper carbonate hydroxide

Sample	Interplanar spacing of copper carbonate hydroxide, nm							
	(020)	(120)	(220)	(20-1)	(21-1)	(041)	(250)	(061)
PDF No. 41–1390	0.5970	0.5040	0.3690	0.2861	0.2781	0.2185	0.2128	0.1689
5 days	–	–	–	–	–	–	–	–
30 days	0.5990	0.5048	0.3691	0.2853	0.2747	0.2183	0.2131	0.1705
45 days	0.5990	0.5048	0.3691	0.2849	0.2770	0.2183	0.2131	0.1683
60 days	0.5990	0.5048	0.3697	0.2858	0.2762	0.2182	0.2134	0.1691
5 years	0.6018	0.5071	0.3705	0.2860	0.2785	0.2196	0.2136	0.1691

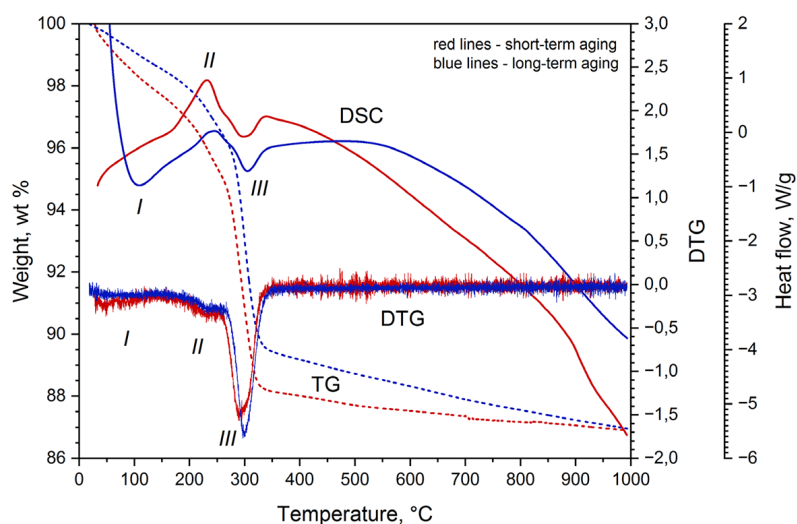


Fig. 2. DSC/DTG/TG curves of nanostructures produced by non-equilibrium electrochemical copper oxidation

The temperature of Cu_2O oxidation to CuO (peak *II*) changes from 231.3 to 245.2 °C whereas the temperature of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ decomposition changes from 298.2 to 304.7 °C (peak *III*).

The overall weight loss of nanostructures of copper compounds is 13 wt.% after both short-term and long-term aging. Comparison of the weight loss integral and differential curves reveals that after long-term aging the temperature range of the second $\text{Cu}_2(\text{OH})_2\text{CO}_3$ decomposition stage is narrower than at short-term aging. Because of this, it seems that long-term aging causes greater weight loss during the $\text{Cu}_2(\text{OH})_2\text{CO}_3$ decomposition.

Electrochemical aluminum oxidation

The structure of aluminum oxidation product (boehmite AlOOH , No. 17–0940) is not significantly changed at long-term aging (Fig. 3). Also, the shape and width of the peaks is not changed. The difference in the intensities of the (120), (031), (051) peaks indicates the anisotropy of the particles. As a result, the samples used to XRD analysis consist of the particles with different dominant faces.

Comparison of TG/DTG/DSC curves during heat treatment of the products of aluminum electrochemical oxidation is shown in Figure 4. At short-term aging, weight loss is 24.87 %. At

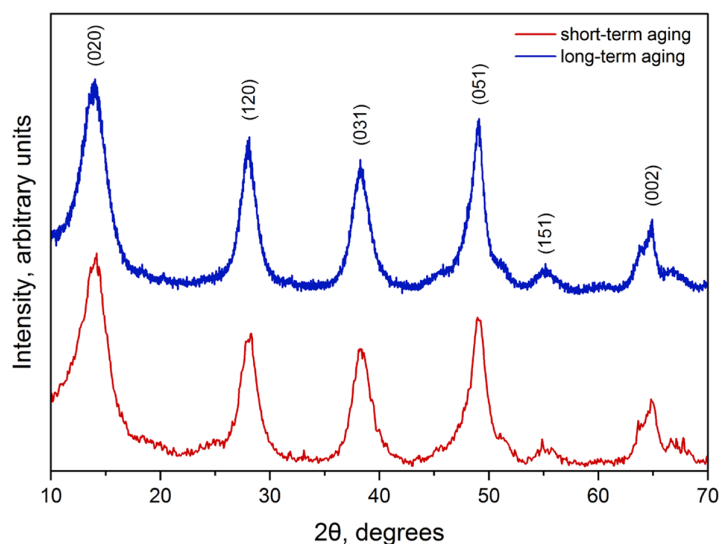


Fig. 3. XRD patterns of the nanostructured powders produced by electrochemical oxidation of aluminum

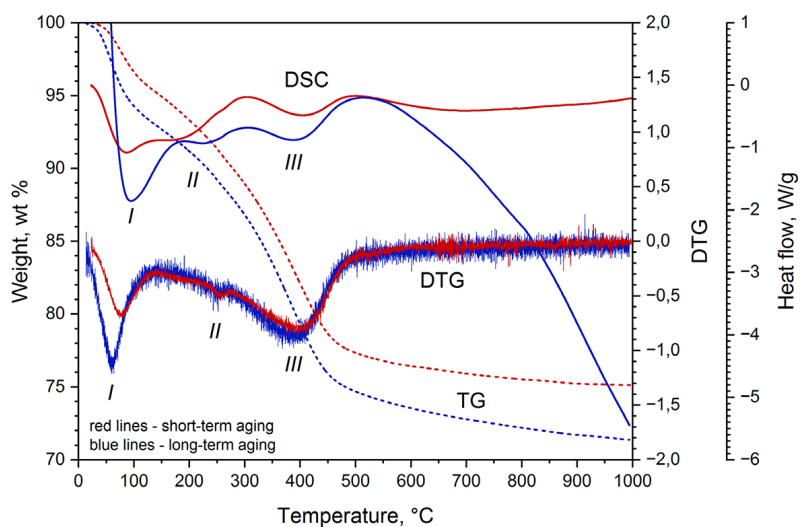


Fig. 4. DSC/DTG/TG curves of nanostructures produced by non-equilibrium electrochemical aluminum oxidation

Table 4. Endothermic effects of DSC curves of boehmite

Aging	<i>I</i>	<i>II</i>	<i>III</i>
Short-term aging	72	180	403
Long-term aging	94	225	390

long-term aging it increases to 28.63 % because of physical sorption of atmospheric moisture and compounds. The longer the duration of the aging process the more sorption.

The sharpest weight change is observed at temperatures up to 100 °C. Endothermic effects (peak *I*) at a temperature of 72 °C (short-term aging) and 94 °C (long-term aging) correspond to this weight loss. The removal of moisture at higher temperatures is the result of decrease in the reactivity of the nanomaterial due to a change in the structure ordering. The comparison of the heat flow reveals that the temperatures of boehmite decomposition increase by 20–45 °C after long-term aging (Table 4, peaks *II* and *III*). It is due to some transformations of nanostructured products of electrochemical aluminum oxidation.

Conclusions

In this paper, the evolution of the nanostructured materials produced by separate electrochemical oxidation of copper and aluminum has been considered. The XRD measurements showed a peak shift of all copper-containing compounds (copper (I) oxide, copper (II) oxide and copper carbonate hydroxide $\text{Cu}_2(\text{OH})_2\text{CO}_3$) to the large values of the interplanar distance. It has been assumed that the increase in interplanar distances is related to the interaction of nanostructures with oxygen and CO_2 of the atmosphere. TG/DTG/DSC measurements of the aluminum electrochemical oxidation products showed that the weight loss is 24.87 % at short-term aging, whereas it increases to 28.63 % at long-term aging because of physical sorption of atmospheric moisture and compounds. Transformations of nanostructured products of electrochemical aluminum oxidation can cause an increase by 20–45 °C in the temperature of boehmite decomposition after long-term aging. Generally, we can state a significant evolution of the products of separate copper and aluminum electrochemical oxidation over time.

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