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Solution transformation of the products of AC electrochemical metal oxidation

N.V. Usoltseva^{*}, V.V. Korobochkin, M.A. Balmashnov, A.S. Dolinina

Department of Chemical Engineering, National Research Tomsk Polytechnic University, Lenin avenue, 30, Tomsk, 634050, Russia

Abstract

Electrochemical oxidation of copper and aluminium using alternating current of industrial frequency results in the formation of non-equilibrium products. Their transformations during the ageing in sodium chloride solutions of different concentrations have been considered. According to X-Ray diffraction confirmed by TG/DSC/DTG analysis, irrespective of solution concentration, the ageing products consist of aluminium oxyhydroxide (boehmite, AlOOH), copper-aluminium carbonate hydroxide hydrate (Cu-Al/LDH) and copper chloride hydroxide (Cu₂(OH)₃Cl). The increase of the solution concentration leads to Cu₂(OH)₃Cl formation and makes difficulties for metal oxide carbonization to Cu-Al/LDH. Ageing in highly diluted solution contributes not only to Cu-Al/LDH formation but also boehmite hydration that is verified by IR-spectra. The pore structure characteristics have been also discussed. They do not significantly depend on phase composition and vary in ranges of 161.2–172.6 m²/g (specific surface areas), 0.459–0.535 cm³/g (total pore volumes). Pore size distributions reveal that a pore structure is predominantly formed by pore with the sizes from 3 to 22 nm; 3.6 nm is the size of pores with the largest pore volume.

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1. Introduction

Metal oxides constitute the largest share of powdered nanomaterials. Among the methods to obtain functional metal oxide materials the special attention is paid to non-equilibrium syntheses¹⁻⁴. Electrochemical metal oxidation

^{*} Corresponding author. Natalya V. Usoltseva Tel.: +7-909-538-0423.
E-mail address: usolceva@tpu.ru

by industrial frequency alternating current is used to produce different metal oxide and oxide systems^{5,6}.

Along with other binary systems of metal oxides the copper-aluminium oxide system is widely used in industry^{7,8}.

Power-saturated products of non-equilibrium electrolysis interact with electrolyte ions and carbon-containing air compounds. Layered double hydroxide (LDH) formation is the result of ageing of copper-aluminium oxide system in electrolyte solution⁹. Heat treatment transforms LDH to the highly active homogeneous mixed oxide system that possesses a number of features (great specific surface area, dispersion and sintering stability) supporting its use in catalytic and sorption processes^{7,10-12}.

Thus, the work is aimed at investigating the solution transformation of the products of AC electrochemical oxidation of copper and aluminium.

2. Experimental

Electrochemical metal oxidation by industrial frequency alternating current was carried out in an aqueous solution of sodium chloride of analytical grade 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. PDF 2 database was used to identify the phase composition.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on thermal analyzer SDT Q600 in air at a heating rate of 10°C min⁻¹ in the temperature range from ambient to 1000 °C.

The FT-IR spectra were recorded on Nicolet 5700 equipped with a diffuse reflectance cell using pressed KBr pellets in the range of 4000–400 cm⁻¹ at resolution of 4 cm⁻¹.

The surface area of the particle was determined from the nitrogen adsorption-desorption isotherms (Brunauer-Emmett-Teller method) at 77 K with TriStar II 3020 gas adsorption analyzer (Micromeritics, USA). The cross-section of the nitrogen molecule was assumed to be 0.162 nm². The total pore volume was calculated at relative N₂ pressure (P/P₀) of 0.999.

The product of ac-oxidation of copper and aluminum in sodium chloride solution with a concentration of 3 wt. %¹³ is divided into three parts. The processing conditions and sample designations are given in Table 1.

Table 1. The processing conditions of the ageing of the products of AC electrochemical oxidation of copper and aluminium

Sample	Experimental conditions
CA-I	Washing from the electrolyte ions by decantation. The sample is kept in highly diluted solution at the ageing.
CA-II	Ageing in the electrolyte solution in which the electrolysis was carried out (3 wt. %).
CA-III	Aging in the solution with a concentration of 15 wt. % obtained by adding powdered sodium chloride to a suspension of the electrolysis product in the electrolyte solution.

3. Results and discussion

Irrespective of the condition of electrolysis product ageing in the electrolyte solution, the aging products consist of aluminium oxyhydroxide (boehmite, AlOOH, JCPDS 17-0940), copper-aluminium carbonate hydroxide hydrate (Cu_{2.5}Al₂C_{1.7}O_{8.9}·5.2H₂O, Cu-Al/LDH, JCPDS 46-0099) and copper chloride hydroxide (Cu₂(OH)₃Cl, JCPDS 25-1427) (Figure 1a). The increase of the solution concentration intensifies copper oxide interaction with the dissolved sodium chloride resulting in the formation of copper hydroxychloride Cu₂(OH)₃Cl. Primary binding of copper into Cu₂(OH)₃Cl causes the decrease in copper part that participates in Cu-Al/LDH.

Air ageing in electrolyte solution results in the absorption of dissolved carbon dioxide by nano-sized copper-aluminium oxide system due to high affinity of carbonate ions to some oxyhydroxides. Aluminium carbonate and aluminium carbonate hydroxide are unstable because they are completely hydrolyzed to sparingly soluble

aluminium hydroxide. The most intensive carbonization occurs in solutions containing carbonate ions, but the adsorption of air carbon dioxide also takes place¹⁴. In highly concentrated solutions the copper chloride hydroxide is preferably formed mainly because the concentration of chloride ions is much higher than of carbonate ions. In addition, the solubility of air carbon dioxide is decreased with the increase of sodium chloride concentration¹⁵.

At the ageing of electrolysis product in highly diluted solution (CA-I) boehmite is partially hydrated. It leads to the increase in the lattice parameters as evidenced by overlapping the most intense reflections of boehmite and Cu-Al/LDH. It is less typical for the sample ageing in solution with a concentration of 3wt. % (CA-II).

Weight loss of the samples CA-I, CA-II and CA III (4.4, 4.5 and 5.0 wt. %, respectively) and endo effects at the temperatures up to 110°C correspond to the emission of the free moisture from all samples and bound moisture from the samples CA-I and CA-II (Figure 1b). Decomposition of Cu-Al/LDH to copper oxide CuO and boehmite occurs in the temperature range of 110-150°C and of $\text{Cu}_2(\text{OH})_3\text{Cl}$ in the temperature range of 230-270°C. $\text{Cu}_2(\text{OH})_3\text{Cl}$ decomposition in the sample CA III requires higher temperatures (240-290°C) because in a more concentrated solution the compound of increased stability is formed. In all samples endo effect and the corresponding peak of the mass loss in the temperature range of 200-470°C that is overlapped by the peaks from decomposition of other compounds, correspond to the boehmite decomposition to α -alumina.

IR spectroscopy is used to clarify the boehmite structure (Figure 2). A wide range of stretching OH vibrations ($3800\text{--}2000\text{ cm}^{-1}$) is caused by the high sensitivity of electron cloud of OH bond to intermolecular interaction. The position of adsorption bands depends on the strength of the hydrogen bond formed by OH groups¹⁶. There are three kinds of hydroxide ions on the boehmite surface. One of them is situated on ribs and connected with one aluminium cation. Two other kinds of hydroxide ions are located on faces and connected with two and three aluminium cations. The increase of coordination of oxygen ion via aluminium leads to the decrease of the frequency of stretching OH vibrations. Hence, hydroxyls connected with one aluminium cation are characterized by stretching vibration of 3660 cm^{-1} . It is not possible to identify this bend with our IR spectrum because of its low intensity. Bands with the maxima at 3300 and 3100 cm^{-1} correspond to stretching vibration of hydroxyls connected with two and three aluminium cations, respectively¹⁷.

The strong band at 1150 cm^{-1} and the shoulder at 1065 cm^{-1} are respectively assigned to asymmetric ($\delta_{\text{as}}\text{ Al-OH}$) and symmetric ($\delta_{\text{s}}\text{ Al-OH}$) bending vibrations of bulk O-H of boehmite, the weak band at 880 cm^{-1} is assigned to stretching vibrations of superficial O-H ($\delta\text{ OH}$). The bands 740 , 620 и 480 cm^{-1} are respectively assigned to symmetric ($\delta_{\text{s}}\text{ Al-O}$) and asymmetric ($\delta_{\text{as}}\text{ Al-O}$) bending vibrations and stretching ($\delta_{\text{as}}\text{ Al-O}$) vibration of aluminium-oxygen bond.⁸

According to²⁷, broad band in the range of $2300\text{--}1800\text{ cm}^{-1}$ is assigned to interlaminar hydrogen bonded OH vibrations of boehmite. Hydrogen bond causes the reduction in OH vibration amplitude and decrease of absorption band intensity of related hydroxyls in comparison with free hydroxyls. Absorption band in the range of $2385\text{--}2340\text{ cm}^{-1}$ is assigned to adsorbed carbon dioxide. Coordinatively unsaturated cation and anion centres of boehmite absorb respectively air water molecules and carbon dioxide in the undissociated form. The set of the absorption bands in the range of $3760\text{--}3720\text{ cm}^{-1}$ is assigned to asymmetric stretching vibrations of water molecules as H-O-H, whereas absorption band in the range of $1725\text{--}1595\text{ cm}^{-1}$ corresponds to their bending vibrations $\delta\text{ H-O-H}$.

Layered double hydroxide in samples I and II was identified by the shoulder of absorption band ($1440\text{--}1300\text{ cm}^{-1}$) at 1350 cm^{-1} that corresponds to asymmetric stretching vibration of interlaminar carbonate $\nu_{\text{as}}(\text{CO}_3^{2-})$. Reduction of the symmetry in interlaminar space is the reason of absorption band shift to longer wavelength (smaller wavenumber) relatively its position of free carbonate ions¹⁹. Also there is increased absorption of carbonate ions in the range of $3450\text{--}3300\text{ cm}^{-1}$ and absorption band at 420 cm^{-1} due to the vibration of metal-oxygen bond in the layer of LDH²⁰.

Irrespective of phase sample composition, the main phase is boehmite that is characterized by a highly developed porous structure⁵. Copper-aluminum carbonate hydroxide hydrate Cu-Al/LDH as a compound from the class of layered double hydroxides has a considerable surface area and pore volume. However, the increase in the content of Cu-Al/LDH reduces the basic characteristics of porous structure due to the boehmite binding²¹.

According to porous structure characteristics of the ac-oxidation products of copper and aluminum, shown in Table 2, the decrease of LDH content and increase of the copper chloride hydroxide content cause the linear growth of the product specific surface area from 161.9 to $172.6\text{ m}^2/\text{g}$. However, the differences do not exceed 3.5 wt. %.

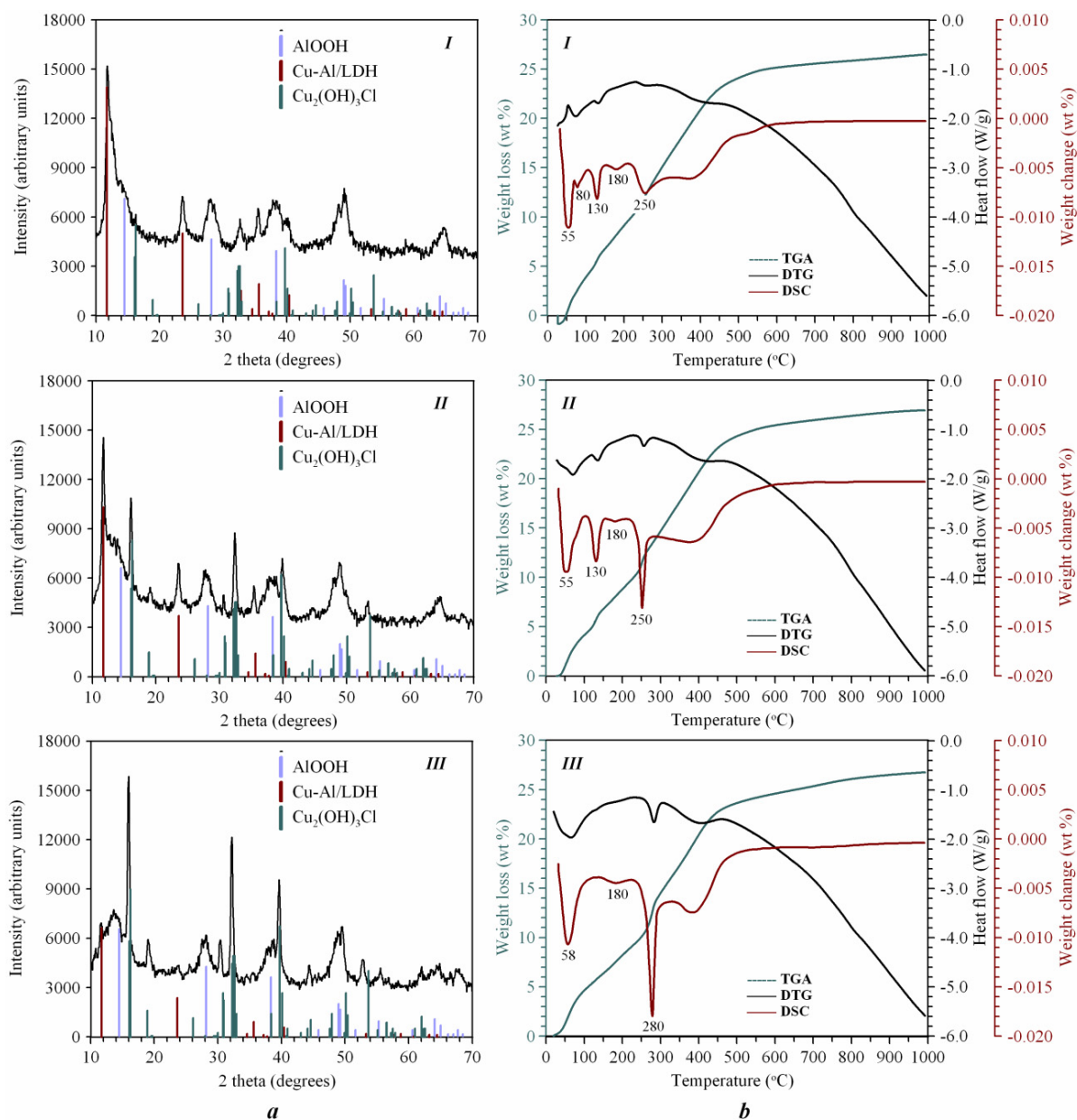


Fig. 1. Powder X-ray diffraction patterns (a) and TG/DSC/DTG curves (b) of the products of AC electrochemical oxidation of copper and aluminium after ageing in sodium chloride solution with concentrations of ~ 0 (I), 3 (II) and 15 (III) wt. %

Table 2. Characterization of the pore structure of the products of AC electrochemical oxidation of copper and aluminium

Sample	Concentration of sodium chloride solution, wt. %	Specific surface area, m ² /g	Total pore volume, cm ³ /g
CA-I	~ 0	161.9	0.459
CA-II	3	167.2	0.545
CA-III	15	172.6	0.535

The pore volume reaches a maximum for a sample with a high content of both copper-containing products of ageing – $\text{Cu}_2(\text{OH})_3\text{Cl}$ and Cu-Al/LDH . Mixed dynamics in the porous structure characteristics indicates a change in the pore size distribution and determining role of the boehmite structure in the formation of the material porous structure.

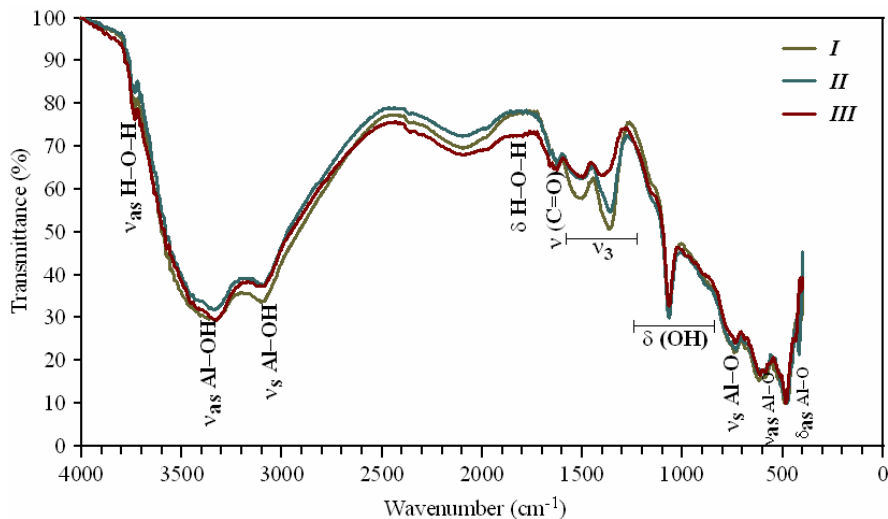


Fig. 2. IR spectra of the products of AC electrochemical oxidation of copper and aluminium after ageing in sodium chloride solution with concentrations of ~ 0 (I), 3 (II) and 15 (III) wt. %

The relatively low values of specific surface area and total pore volume of the sample ageing in highly diluted solution is due to the abovementioned boehmite hydration. It results in the occupation of some pores that become unavailable for the adsorbent in the process of analyzing the porous structure characteristics. It is seen from the pore size distribution, shown in Figure 3, that the volume of pores with size of 3.6 nm in the sample CA-I is 11 wt. % less than in the other samples. Furthermore, the pore volume of the sample CA-I in the range of 6.7-21.8 nm is 15-35 wt. % lower than for samples ageing in more concentrated solutions. The differences of the porous structure characteristics of the samples CA-II and CA-III are due to the pore size distributions. The aging of the sample in a solution with a concentration of 15 wt. % leads to the formation of a product possessing a larger pore volume with sizes of 2.8 and 3.2 nm and a smaller volume of pores with sizes of 7.86 and 9.64 nm. The pores having sizes of 2.8 and 3.2 nm cause higher specific surface, whereas a smaller volume of pores having sizes of 7.86 and 9.64 nm is the reason for the lower value of the total pore volume of the sample.

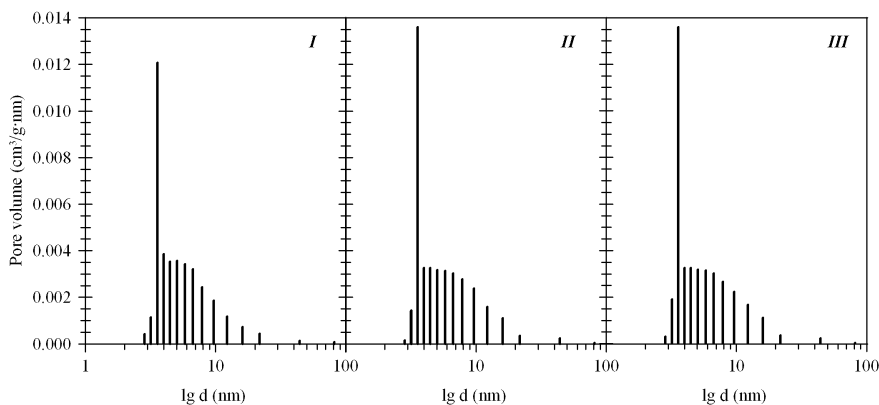


Fig. 3. Pore size distributions of the products of AC electrochemical oxidation of copper and aluminium after ageing in sodium chloride solution with concentrations of ~ 0 (I), 3 (II) and 15 (III) wt. %

4. Conclusion

Investigation of solution transformation of non-equilibrium products of AC electrochemical oxidation of copper and aluminium shows that the ageing of electrolysis products in sodium chloride solutions results in the carbonization to copper-aluminium carbonate hydroxide hydrate (Cu-Al/LDH) and chlorination to copper chloride hydroxide (Cu₂(OH)₃Cl). The increase of the solution concentration leads to Cu₂(OH)₃Cl formation and makes difficulties for metal oxide carbonization to Cu-Al/LDH. Ageing in a highly diluted solution contributes not only to Cu-Al/LDH formation but also boehmite hydration that is verified by IR-spectra. Pore structure characteristics do not significantly depend on the phase composition and vary in ranges of 161.2–172.6 m²/g (specific surface areas), 0.459–0.535 cm³/g (total pore volumes). Pore structure of the products of AC electrochemical oxidation of copper and aluminium is predominantly formed by pore with the sizes from 3 to 22 nm; 3.6 nm is the size of pores with the largest pore volume.

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