

Plasma dynamic synthesis of ultradispersed copper oxides

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Abstract. Copper oxide is necessary material for production of superconductors. The issue of obtaining high purity and nanosides CuO is actual. This article shows the results on the obtaining of nanodispersed copper oxide by plasma dynamic method in system based on coaxial magneto plasma accelerator with copper electrodes. Such analyses of ultradispersed synthesized products as X-Ray diffractometry, IR-spectroscopy and thermal analysis were carried out. According to XRD such phases as copper Cu, copper oxide (I) Cu₂O, copper oxide (II) CuO, and copper hydroxide hydrate Cu(OH)₂•H₂O were identified in the product. It was found that with the gradual heating of the initial product up to 800 °C the phase content changed dramatically in terms of enhancing copper oxide phase (up to 97%).

1. Introduction

Nanodispersed copper oxide (CuO) is widely used in catalysis [1], high critical temperature superconducting [2] applications due to its excellent physical and chemistry properties and cost effectiveness [3-6]. Copper oxide is one of the main components of yttrium-barium cuprates composition. This material has unique property to reach zero electrical resistance at certain temperature and convert to superconductive state. Using this property it is possible to create effective systems of production, accumulation and transfer of electrical energy over long distances, super-power generators, high-speed magnetic levitation transport, and powerful magnet systems for thermonuclear reactors, particle accelerators, super-fast computers and ultrasensitive diagnostic devices. The main advantage of CuO in comparison with Cu₂O is the stability. The CuO is stable at room temperature (Cu ion is in the +2 valance state) whereas Cu₂O (+1 valance state) is only stable above 1020 °C. In general, all methods of obtaining nanodispersed copper oxide (II) are chemical-based techniques. In this paper, the possibility of obtaining nanodispersed copper oxide by plasma dynamic method is shown.

2. Materials and Methods

The basis of plasma dynamic synthesis is the use of a high-current pulsed coaxial magneto-plasma accelerator (CMPA) of erosion type with copper central electrode and barrel-electrode [7-8]. Pulse power supply is provided to CMPA from the sectioned capacitive energy storage with the total capacity of 57.6 mF and the charging voltage $U \leq 5.0$ kV. The CMPA consists of two main components: the removable one is a classic coaxial Z-pinch accelerator and the stationary one is an external induction system. The use of copper electrode and the copper accelerating channel (barrel) allow to realize the synthesis of nanodispersed copper oxides.

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The principle of the accelerator operation is as follows. Initially, the CMPA is included in the discharge circuit of capacitive energy storage. With the closure of the power keys the discharge current begins to flow from the capacitor bank to the inductive load. At achievement of a certain level by the discharge current, there is an arc discharge with plasma structure of Z-pinch type with circular plasma bridge. The plasma structure stable state is provided by the magnetic field pressure of its own current and the magnetic pressure from axial component of an external magnetic field from the solenoid induction system.

Electro erosive recovery of material from the copper surface of the acceleration channel occurs when the plasma flows through this channel. Copper is involved into the discharge structure, converted into the plasma state and removed from the accelerating channel at hypersonic speeds in a closed space of the chamber. The chamber is filled with a mixture of gaseous oxygen. Thus, the main precursors of oxidative processes interact in the chamber.

The registration of energy parameters $u(t)$ and $i(t)$, was carried out using active voltage divider and Rogowski transformer. Their signals were recorded using a digital oscilloscope Tektronix. Typical oscillograms of discharge current $i(t)$ and voltage $u(t)$ are shown in figure 1. Using these oscillograms the discharge power curve was built. By its integrating the value of input to the CMPA energy (figure 1) was found. It should be noted the whole process is no much longer than 500 μs .

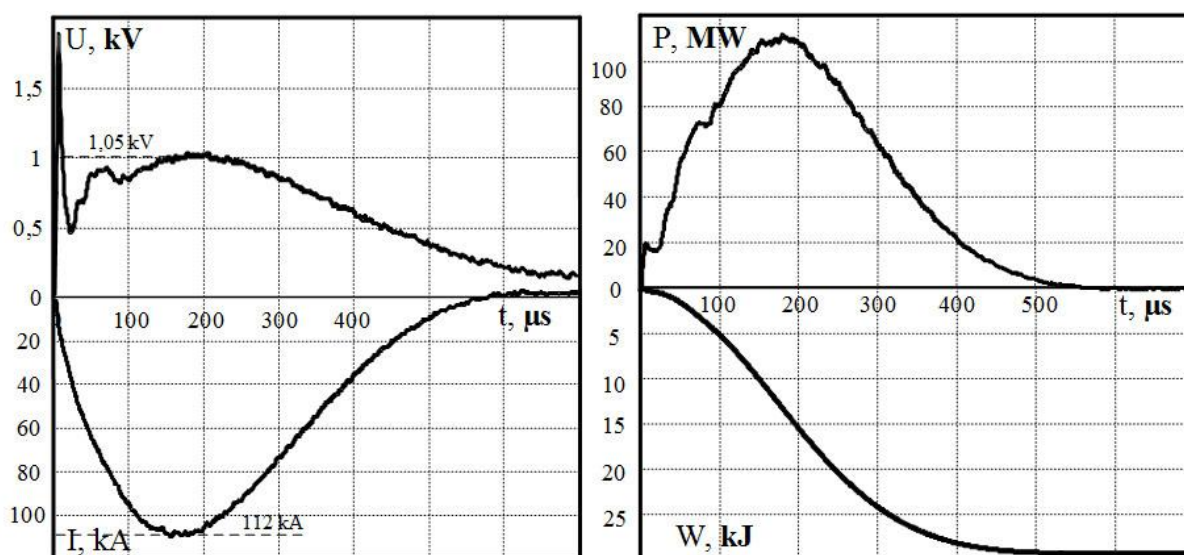


Figure 1. Typical oscillograms current $i(t)$, voltage $u(t)$ and curve power $p(t)$ and energy $w(t)$.

The collection of the resulting product was made after waiting few hours. The phase composition of the resulting plasma dynamic synthesis product was studied by X-ray diffractometry (XRD) with using diffractometer Shimadzu XRD7000 having copper cathodes ($\text{CuK}\alpha$ -radiation). The initial product was annealed using high-temperature oven Nabertherm 1800/3 at temperature of 420 $^{\circ}\text{C}$, 600 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$. Also the synthesized product was analyzed by IR-spectroscopy (Nicolet 5700), mass spectrometry (TRACE DSQ (GC / MS)) and thermal analysis (combined TGA / DSC / DTA analyzer SDT Q600).

3. Results and discussion

Figure 2 shows XRD patterns of initial and annealed products. The software PowderCell 2.4 with the structural database PDF2+ was used to analyze XRD-patterns. According to the diffraction pattern (Figure 2a) of initial powder it is the heterophase product. The dominant phase is copper oxide CuO with an average size of coherent scattering regions (CSR) of about 14 nm. It should be noted the final product also has several nanocrystalline phases (copper oxide (I) Cu_2O , copper Cu , copper hydroxide

hydrate $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$). Table 1 shows the percentage of crystalline phases in the product. XRD-pattern of the powder, heated in air up to $420\text{ }^\circ\text{C}$ at a rate of $80\text{ }^\circ\text{C}/\text{min}$ with the exposure of 30 min and followed natural cooling down to the room temperature is presented in figure 2b. It unambiguously indicates the fully disappearance of strong small angle reflection and other reflections corresponded to the phase of copper hydroxide hydrate $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$. The formation of this phase can be explained by the presence of air humidity in the chamber. After being heated, it is decomposed to copper oxide CuO and the water that evaporates, ensuring irreversibility of process. Due to this, the percentage of CuO is increased up to 86.0%, according to the change in the ratio of the coherent reflection intensities of the remaining phases. However, X-ray amorphous component is still present in the product.

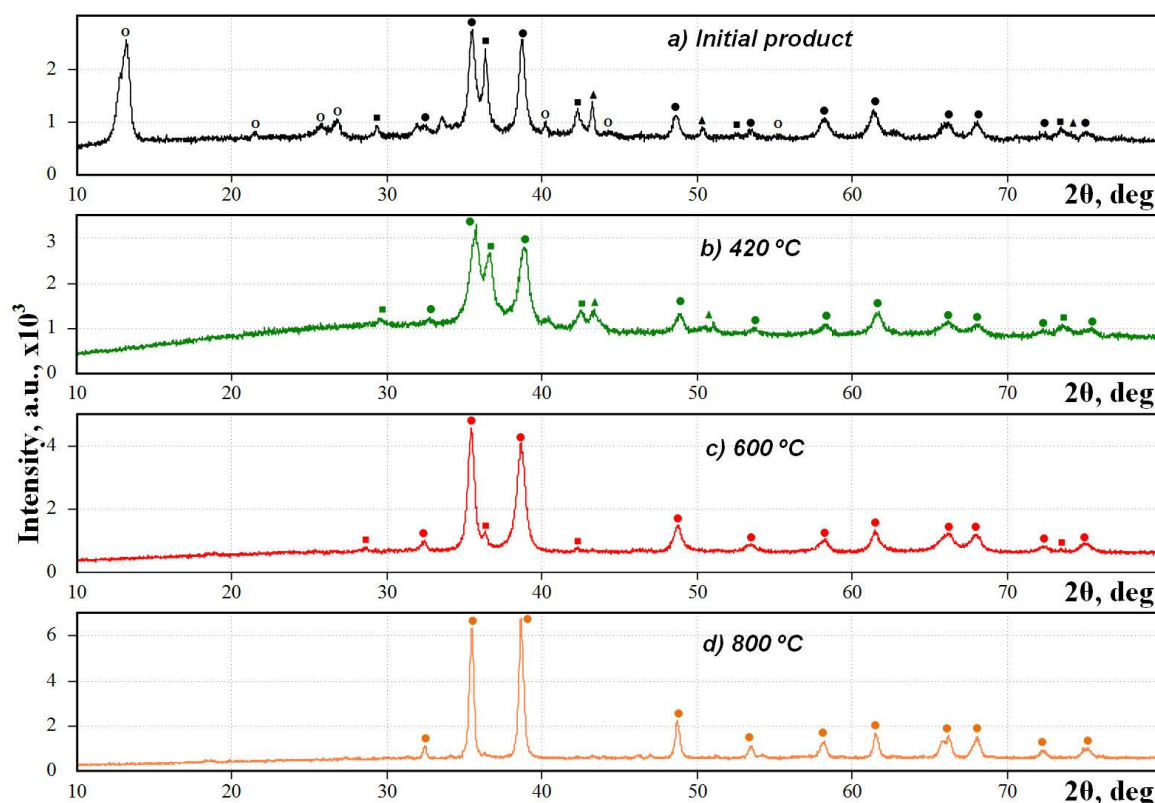


Figure 2. XRD patterns of the plasma dynamic synthesis product and its evolution under the temperature influence.

● CuO ; ■ Cu_2O ; ▲ Cu ; ○ $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$

Table 1 - Ratio in weight % of crystalline product components.

Product	CuO (C2/c (15), monoclinic)	Cu_2O (Pn-3m (224), cubic)	Cu (Fm-3m (225), cubic)	$\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (P*, -1, anorthic)
Initial	48%	25%	7%	20%
420 °C	86%	9%	5%	-
600 °C	91%	7%	2%	-
800 °C	97%	2%	~1%	-

The figures 2c and 2d show XRD-pattern of product annealed with the same parameters (rate and exposure) to the temperature of $600\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$, respectively. The XRD-pattern of the resulting material is characterized by the almost complete disappearance of the reflections of the crystal copper

and consistent reducing the intensity of reflections of Cu_2O to the level of "traces". In addition, there is a significant reduction of x-ray amorphous component after the high-temperature heat treatment. A significant decrease in the broadening of the strongest reflections CuO indicates the recrystallization process in the temperature range of about 400-800 °C, the growth of CSR and hence the crystallite sizes of this phase. Calculations show an increase of the CuO mass content up to 97.0% (table 1), increase of this phase CSR up to ~ 100 nm.

Using IR-spectroscopy the initial copper-containing plasma dynamic synthesis product and the sample after heat treatment in air at 420 °C were studied. Initial sample IR-spectrum is shown in the figure 3. This spectrum is characterized by an intense absorption band with a maximum at 3471 cm^{-1} and a shoulder at 3253 and 3186 cm^{-1} due to stretching vibrations of water molecules and the structural hydroxyl groups [9, 10]. The absorption bands with maxima at 2958 , 2925 and 2855 cm^{-1} can be attributed to the stretching vibrations of OH-groups. The absorption band of low intensity at 1660 cm^{-1} is explained by the deformation vibrations of the OH group. According to the literature [11], even momentary contact of freshly prepared nanoparticles of copper-containing powder with air environment with relative humidity of 58-60% is accompanied by the formation of hydroxyl hydrate cover. The sorption of water molecules on the copper containing particles is accompanied with both the dissociation with the formation of surface hydroxyl groups and the localization of the water molecules on the surface of the nanoparticles in the coordinated state. In the range of 2516 - 2196 cm^{-1} of the initial sample IR-spectrum there are absorption bands of adsorbed molecules of CO_2 . As a result of the carbon dioxide sorption on the surface of the nanoparticles hydroxycarbonate cover $\text{Cu}_2\text{CO}_3(\text{OH})_2$ can be formed [11]. Its presence is manifested in the range of 1582 - 1247 cm^{-1} with the intensity absorption bands that are typical for carbonate structures of monodentate type. The absorption band at 738 cm^{-1} is also can be explained by vibrations of the carbonate ion. Absorption bands in the 592 - 430 cm^{-1} indicate the presence of copper oxide CuO , absorption bands at 874 and 678 cm^{-1} are due to deformation vibrations of Cu-O-H [12].

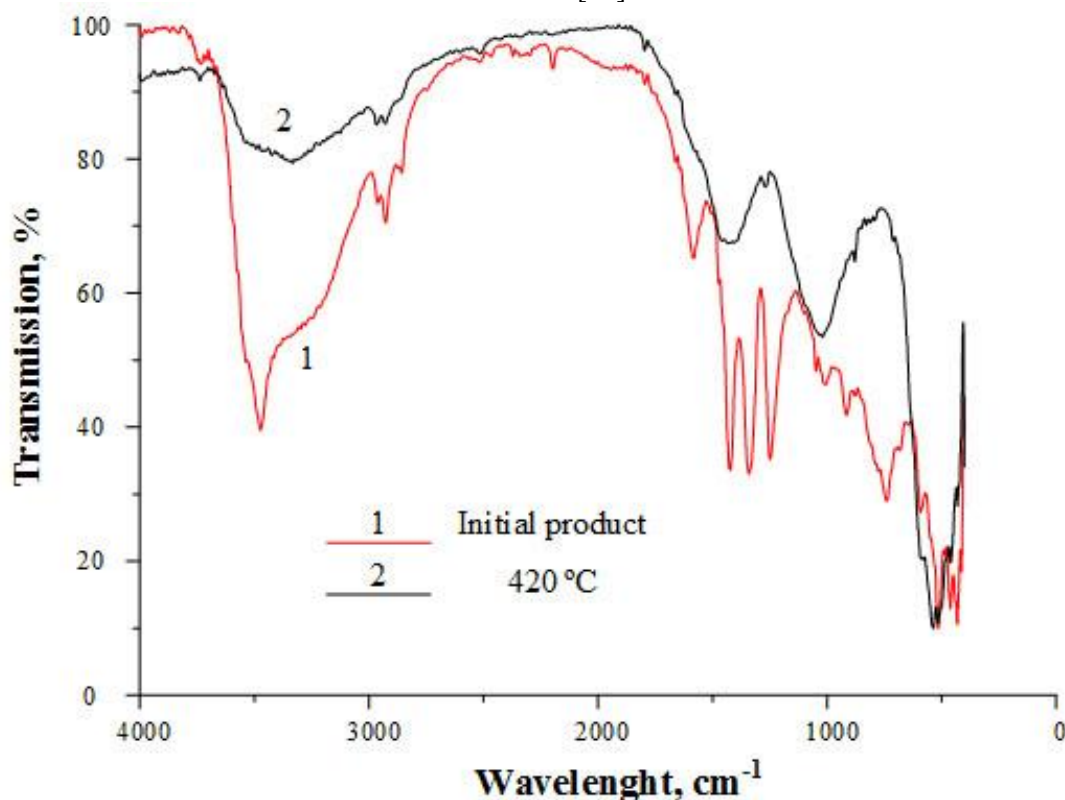


Figure 3. IR-spectra of the copper-containing products of plasma dynamic synthesis: 1 - initial powder, 2 - powder after heating treatment in air at 420 °C.

The results of thermographic investigations of the initial dispersed synthesis product obtained by linear heating of sample with mass of 5.478 g in air at 10 °C/min are shown in Figure 4. The character of TG-curve shows that at heating up to 1000 °C there is a decrease in sample mass by 19.5%. At a temperature range up to 650 °C several intervals of consistent reduction of the derivative changes in the mass of the sample are clearly distinguished. Such uneven weight reduction of the sample with increasing of temperature occurs simultaneously with the appearance on the DSC-curve of exothermic peaks at 242 °C extremes, 321 °C, 431 °C and 500 °C, coincides with the boundary of said intervals. Results of mass-spectrometric synchronous measurements show that after heating of the sample up to 800 °C there is a removal of the adsorbed on the particle surface gases of nitrogen and oxygen: in mass spectrum there are peaks with mass numbers of m/z equal to 28 and 32. Upon further heating the crystallization water is removed.

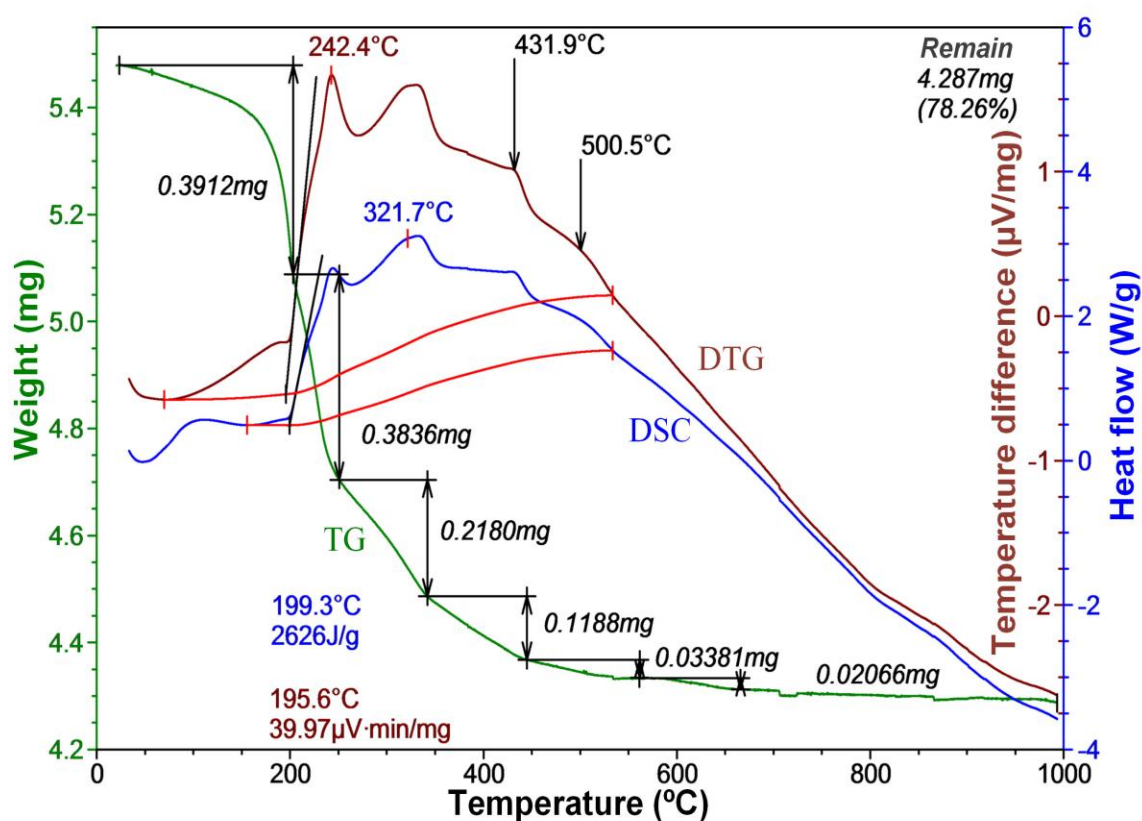


Figure 4. The data of thermographic studies

The main weight reduction upon heating the sample to about 450 °C is connected with the decomposition of hydrated copper hydroxide, as shown by XRD. In the temperature range of 200-280 °C in parallel with the endothermic decomposition reaction of $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ flows the similar process of decomposition of copper hydroxycarbonate $\text{Cu}_2\text{CO}_3(\text{OH})_2$. Its presence in the plasma dynamic synthesis product is determined according to IR-spectroscopy (Figure 3) and mass spectrometric measurements in the temperature range of 200-250 °C with the presence of a peak with a mass number $m/z=44$, corresponded to the carbon dioxide emissions. Small endoeffects caused by the decomposition reaction of the copper compounds, completely overlap by exothermal effects due to the oxidation of copper metal to oxide Cu_2O and further oxidation of the formed and present in the initial product Cu_2O to CuO . The growth of mass of the sample due to the oxidation process is very small in comparison with the loss by the above mechanism.

4. Conclusions

The paper shows the possibility of direct plasma dynamic synthesis of nanodispersed copper-containing powders using a high-current coaxial magneto plasma accelerator of erosion type. Components of the powder obtained by plasma dynamic method are metallic copper, copper oxides Cu₂O and CuO, as well as hydrated copper hydroxide Cu(OH)₂•H₂O. Using XRD analysis, IR spectroscopy and thermal analysis the changes in the composition of the synthesis product are investigated by heating it in air. The heat treatment of the synthesized powder at 800 °C in air allow to yield the nanodispersed product with the main crystal phase of copper oxide CuO (97 %).

Acknowledgements

The work was supported with the Russian Science Foundation (project # 15-19-00049).

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