

# Characterization of copper nanopowders after natural aging

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**Abstract.** Copper nanopowders after storage under natural conditions can oxidize and change their properties. In this work, the phase composition, morphology and thermal properties of copper nanopowders after natural aging of 10 years were studied. The copper nanopowders were produced by the method of electrical explosion of wires in different gaseous ambient: argon and carbon dioxide. The nanopowders were characterized by X-ray diffraction, thermal analysis, scanning electron microscopy, Fourier transform infrared spectroscopy. The content of copper oxides phases was found to be increased in comparison with freshly synthesized powders. This transformation results in the change of the thermal characteristics of the nanopowders. The effect of the synthesis conditions on the composition and thermal characteristics was shown.

## 1. Introduction

In recent years, copper nanopowders (Cu NPs) have attracted much attention due to their catalytical, optical, tribological and electrical properties [1–4]. The problem in Cu NPs application is their high activity with oxygen atoms and rapid oxidation during handling and storage under ambient conditions that results in changes phase composition, morphology and functional properties [5–7].

At present, Cu NPs are prepared using a number of methods, including vacuum vapor deposition [8], metal vapor synthesis [9], thermal reduction [10], chemical reduction [11], and laser ablation [5]. Among these methods, electrical explosion of wires is known to be a promising method for the synthesis of nanoscale powders [12–14]. The metal nanopowders produced by EEW are characterized by a high chemical reactivity at high temperatures and a high stability during their storage. To achieve the high stability of NPs produced by EEW towards oxidation, a passivation of freshly synthesized powders by slow oxidation in air should be carried out [12–15]. In our previous work, the characteristics of aluminum NPs produced by EEW and stored under ambient conditions for a long time were investigated [16]. It was shown that aluminum NPs remain to be stable toward oxidation with time that was explained by the formation of the oxide-hydroxide layer on the particles surface at passivation. Cu NPs have the properties different from those of aluminum NPs.

The properties of Cu NPs freshly synthesized by EEW were intensively investigated [13, 17]. It is known that they have a specific surface area of 5-10 m<sup>2</sup>/g, a wide particle size distribution in the range from 100 to 4000 nm. The metallic copper content in the particles can vary from 80 to 95 %. The surface of the particles is covered with oxide layer having the thickness of 5-15 nm. Cu NPs stored under ambient conditions are oxidized; during this process a growth of the oxide layer thickness on the particles surface occurs to 30-35 nm for 3 years [17] and the degree of crystallinity of oxides increases. Full oxidation of fine particles is possible.



The changes in the physicochemical properties and phase transformation occurring in Cu NPs at their long-term storage have been studied insufficiently. At the same time, the studies of the phase composition, morphology and the thermal stability of Cu NPs to oxidation during the storage in air are of interest for practical use, also in term of the safety of nanotechnology. The objective of this work is the investigation of the phase composition, morphology and thermal stability of Cu NPs produced by electrical explosion of wires in argon and carbon dioxide, after long-term storage under ambient conditions.

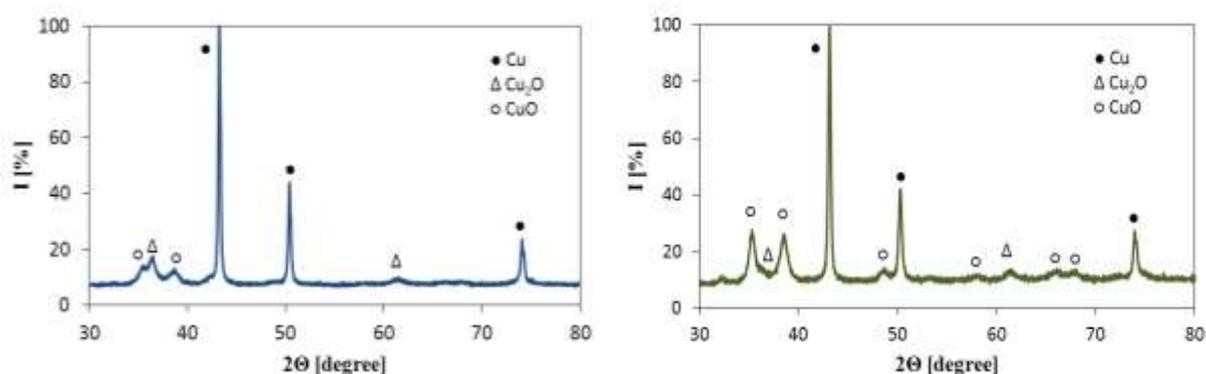
## 2. Experimental

Copper nanopowders were produced by the method of EEW in the following gaseous ambient: argon (the sample Cu(Ar)) and carbon dioxide (the sample Cu(CO<sub>2</sub>)). After production a stabilization of the copper particles surface was carried out by a controlled slow stream of air. The Cu NPs had been stored in the closed containers under natural conditions: temperature 20-25 °C and humidity 60-80 % for 10 years.

The phase composition of the studied Cu NPs was determined by X-ray diffraction (XRD) analysis with CuK $\alpha$  radiation (Shimadzu XRD-7000). The size and morphology of the studied samples were investigated using scanning electron microscope (SEM) JEOL JSM-7500FA. The specific surface area of the samples was determined using a BET-analyzer Sorbi. A thermogravimetric analyzer SDT-Q600 was used to study the thermal gravimetric (TG) and the differential scanning calorimetric (DSC) behavior of the samples from 20 to 1000 °C at a heating rate of 10 °C/min in a flow of air. The infrared spectra of the samples in the spectral range 4000-400 cm<sup>-1</sup> were recorded using Nicolet 5700 Fourier transform infrared (FTIR) spectrometer.

## 3. Results and discussion

The XRD results in figure 1 indicate the presence of crystalline phases of metallic copper and copper oxides Cu<sub>2</sub>O and CuO in the composition of the studied powders. Cu(CO<sub>2</sub>) NP contains more copper oxide CuO in comparison with the sample Cu(Ar) NP, that is caused by the use of oxygen containing gas CO<sub>2</sub> as a medium for fabrication in the process of EEW and partial oxidation of the particles directly in this process.



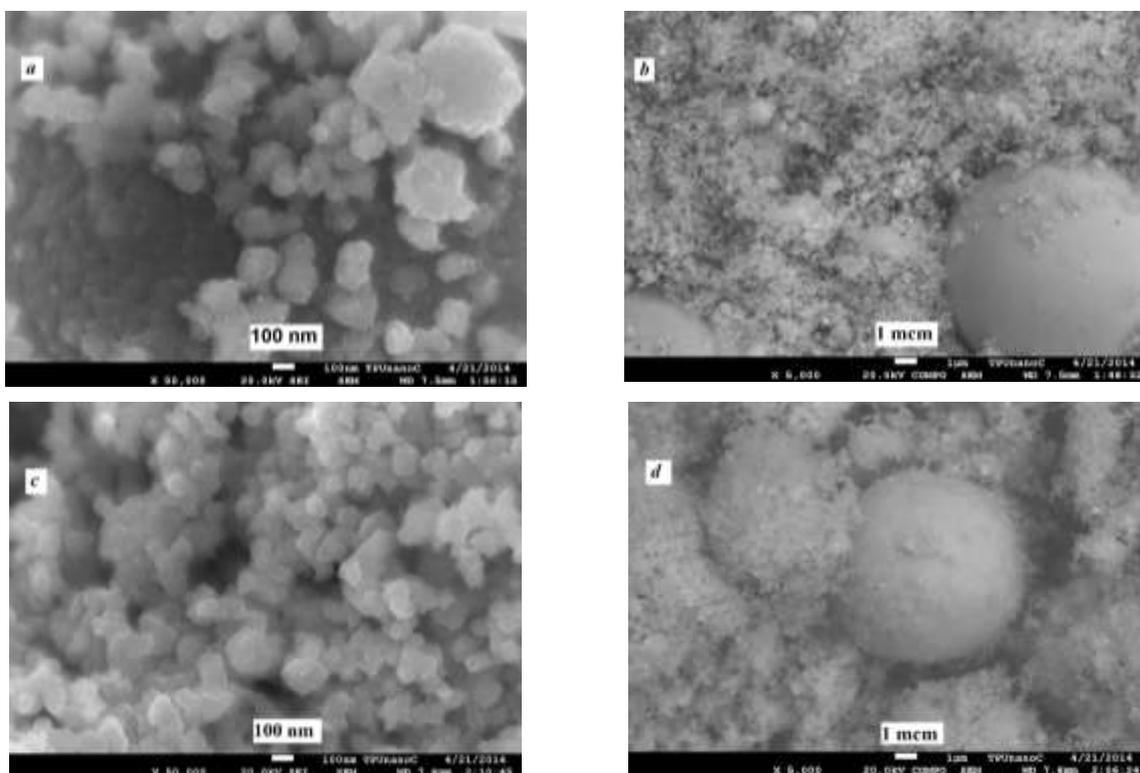
**Figure 1.** XRD patterns of Cu NP: (a) Cu(Ar), (b) Cu(CO<sub>2</sub>).

The average crystallite size of the Cu nanoparticles was estimated using the Debye-Scherrer formula [18] and for the sample Cu(Ar) it was 32 nm, for the sample Cu(CO<sub>2</sub>) - 30 nm.

The specific surface area of the samples Cu(Ar) and Cu(CO<sub>2</sub>) was 6.72 and 5.93 m<sup>2</sup>/g, respectively, which is not much different from that of the freshly prepared Cu NPs.

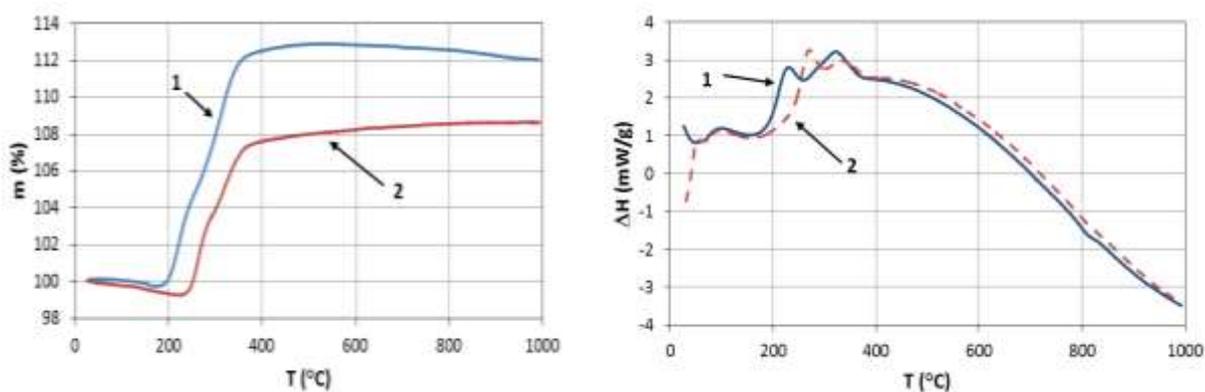
The SEM micrographs of Cu NPs are shown in figure 2. The particles of Cu NPs have a size of about 100-250 nm with a shape close to spherical with friable surface. Among the particles of nanodispersed fraction the particles having the size up to 10 μm with a smooth surface can be found.

It is known that polymodal particles size distribution is typical for all NPs produced by the EEW [12-14]. It can be assumed that nanodispersed fraction of Cu NPs is fully oxidized during long storage in air, which was previously shown in [13, 17].



**Figure 2.** SEM micrographs of Cu NPs: (a), (b) - Cu(Ar); (c), (d) - Cu(CO<sub>2</sub>).

Figure 3 shows the results of thermal analysis obtained at a non-isothermal heating of Cu NPs in air. The desorption of adsorbed gases and water vapor from the surface of the particles occurs in the temperature range 20-200 °C that lead to a weight decrease by about 0.4-0.7 wt. %. This corresponds to the endothermic process on the DSC curve with a minimum at 52.6 °C for the sample Cu(Ar) and 65.7 °C for the sample Cu(CO<sub>2</sub>). Then, after further heating a sharp increase in the weight and heat release occurs as a result of oxidation of the powders. The onset temperature of oxidation is 183 °C for Cu(Ar) NP and 234 °C for Cu(CO<sub>2</sub>) NP.



**Figure 3.** TG (a) and DSC (b) curves for Cu(Ar) NP - 1 and Cu(CO<sub>2</sub>) NP - 2.

The oxidation of Cu NPs occurs in two stages, with maxima in the DSC curve for the sample Cu(Ar) at 225 and 321 °C and for the sample Cu(CO<sub>2</sub>) at 267 and 328 °C. As it was described in [17], a sequential transformation of Cu into oxide Cu<sub>2</sub>O and then into oxide CuO occurs during the oxidation of Cu NPs. The presence of several stages in the oxidation process is typical for nanoscale metals produced by the method of EEW and it is associated with a polymodal particle size distribution and the oxidation of fine particles in the first instance [16].

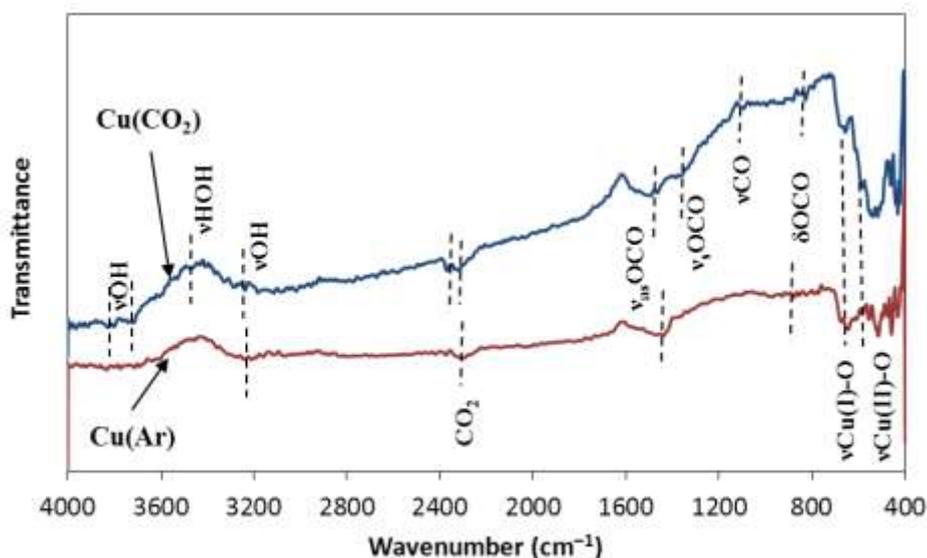
At the first oxidation stage of the sample Cu(Ar) from 183 to 270 °C, metal copper is oxidized to Cu<sub>2</sub>O:  $4\text{Cu} + \text{O}_2 = 2\text{Cu}_2\text{O}$ . The sample weight at this stage is increased by 5.4 wt. %. Further heating of Cu(Ar) NP to 525 °C is accompanied by oxidation of Cu<sub>2</sub>O to CuO by the reaction  $2\text{Cu}_2\text{O} + \text{O}_2 = 4\text{CuO}$  and an increase in the sample weight by 7.8 wt. %. Upon heating in the range of 525-1000 °C, a slight decrease in weight of 0.8 wt. % is observed, due to the partial decomposition of CuO.

The weight of the sample Cu(CO<sub>2</sub>) at the heating to 1000 °C increased by 9.4 wt. %. In the first steps of this sample oxidation in the temperature range from 235 to 300 °C the sample weight increased by 4.3 wt. %. Further heating of the sample up to 1000 °C is accompanied by an increase in the sample weight by 4.1 wt. %.

The specific heat effects during oxidation of the samples Cu(Ar) and Cu(CO<sub>2</sub>) are 904.7 and 750.4 J/g, respectively. The larger thermal effect of the sample Cu(Ar) is caused by a higher content of metallic copper in the composition of this powder, as shown by the XRD results.

According to the thermal analysis data a metallic copper content in the powders is estimated to be 55 % in the sample Cu(Ar) and 35 % in the sample Cu(CO<sub>2</sub>).

The FTIR spectroscopy technique allows obtaining infra spectra of the copper particles surface oxide layer and to examine their state and the composition. Figure 4 shows the FTIR spectra of the studied powders.



**Figure 4.** FTIR spectra of Cu NPs.

The spectrum of the sample Cu(Ar) is characterized by the presence of several absorption bands in the range of 592-430 cm<sup>-1</sup> caused by stretching vibrations νCu(II)-O of copper oxide CuO. The absorption bands with maxima at 643 and 677 cm<sup>-1</sup> can be attributed to the vibrations νCu(I)-O, indicating the presence of oxide Cu<sub>2</sub>O in the composition of the sample [18, 19]. In the spectrum of the sample Cu(CO<sub>2</sub>) the absorption bands in the range of 579-430 cm<sup>-1</sup> typical for copper oxide CuO are observed and the band with a maximum 537 cm<sup>-1</sup> appears. The absorption band at 657 cm<sup>-1</sup> is associated with the presence of oxide Cu<sub>2</sub>O in the sample Cu(CO<sub>2</sub>).

The absorption bands of the adsorbed CO<sub>2</sub> molecules are observed at 2301 cm<sup>-1</sup> in the spectrum of the Cu(Ar) sample and at 2369 and 2322 cm<sup>-1</sup> in the spectrum of the Cu(CO<sub>2</sub>) sample. As a result of carbon dioxide adsorption on the surface of the sample Cu(Ar) carbonate structures are formed, which are characterized by absorption bands due to asymmetric stretching vibrations  $\nu_{as}O-CO$  at 1441 cm<sup>-1</sup> and deformation vibrations  $\delta O-CO$  at 878 and 829 cm<sup>-1</sup> [20]. In the spectrum of the sample Cu(CO<sub>2</sub>) the bands of asymmetric stretching vibrations of the carbonate ion  $\nu_{as}O-CO$  at 1495 and 1466 cm<sup>-1</sup>, symmetric stretching vibrations  $\nu_s O-CO$  at 1336 cm<sup>-1</sup>, symmetric stretching vibrations  $\nu C-O$  at 1096 cm<sup>-1</sup> and deformation vibrations  $\delta O-CO$  at 833 cm<sup>-1</sup> appear.

The numerous low-intensity absorption bands in the range of 3800-3000 cm<sup>-1</sup> in the spectra of the studied Cu NPs are caused by the stretching vibrations of the water molecules and structural hydroxyl groups.

#### 4. Conclusion

The study of the phase composition, morphology and thermal stability of copper nanopowders were carried out after long-term storage under ambient conditions. Copper nanopowders were prepared by the method of EEW in argon and carbon dioxide and then they were stored in the closed containers 10 years. During long storage in the air nanodispersed fraction of the particles was oxidized almost completely due to their high reactivity. The sample Cu(CO<sub>2</sub>) is more oxidized than the sample Cu(Ar). The use of oxygen-containing gas as a medium for a synthesis of powders by EEW results in the obtaining particles finer than in the case of using argon because of the passivating effect. The presence of the smaller particles leads to their more rapid oxidation and smaller metallic copper content in the sample Cu(CO<sub>2</sub>). As a result, the thermal stability of the powder Cu(CO<sub>2</sub>) to the oxidation at the heating is higher than that for the powder Cu(Ar).

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