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Features of the formation of nanoparticles based on copper in thin-layer systems

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ABSTRACT

The paper covers the mechanism of the formation of nanoparticles in thin-layer systems based on citric acid, organic and inorganic copper compounds. It shows the possibility to form copper clusters in the hydrocarbon matrix during heat treatment of the composite layer based on polyethylene and copper acetate.

1. Introduction

Metal nanoparticles are widely used in various fields of science, technology and medicine. Every year the area of their practical use expands. As a rule, the nanoparticles are formed in the fluid media. The treatment of products surface with obtained suspensions allows making a thin layer of nanoparticles. The two-stage nature of thin layers formation from metal nanoparticles, the need to use fluid media can significantly limit the range of products exposed to such a treatment. The question about adhesion of the layers deposited on solid substrates remains unsolved. In this regard, the search for new methods of deposition of thin coatings based on metals or oxides nanoparticles without these limitations is of interest.

In this paper are considered the features of the formation of nanoparticles based on copper in thin coatings deposited by vacuum techniques. The paper continues the earlier studies which showed the possibility to form silver nanoparticles in silver–citric acid bilayer thin-film system [1] during the heating (Fig. 1). The theoretical justification of interaction of citric acid with silver is presented in the works [2,3]. Our interest is to conduct similar research with copper, because of the absence of theoretical research in this area.

2. Experimental

Citric acid coatings were deposited from the active gas phase generated by electron-beam dispersion of acid powder. The electron-beam gun with filamentary cathode which allows to form beams with current density $j = 0.01–0.03$ A/cm^2, energy $E = 0.8–1.6$ keV is used as the electron source. Metal layers were precipitated using resistance method. The average thickness of the deposited citric acid and metal layers were 500 nm and 100 nm, correspondingly. The growth speed during the deposition process was controlled by the quartz crystal microbalance (QCM). The deposition process of layers was produced at initial pressure of residual gases in the vacuum chamber $\approx 4 \cdot 10^{-3}$ Pa. The multilayer systems were formed in one process cycle.

The citric acid (≥99.5%, Aldrich), copper acetate (II) (copper (II) acetatehydrate, 98%, Aldrich), copper chloride (copper (II) chloridedihydrate, ≥99%, Aldrich), polyethylene (linear low density, melt index 1.0 g/10 min (190 °C/2.16 kg); Aldrich), copper (99.5% trace metals basis; Aldrich) and aluminum ((≥99.98% trace metals basis; Aldrich) powders were used as target material.

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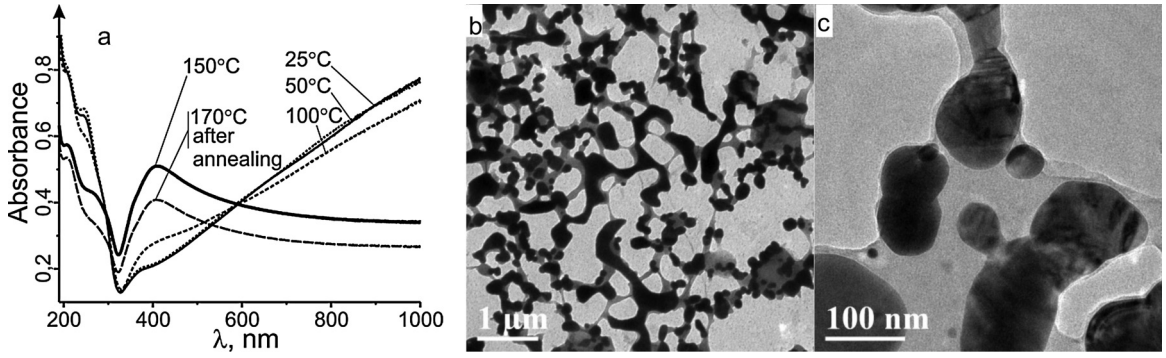

Fig. 1. Silver-citric acid bilayer thin-film system: results of UV–vis spectroscopy (a); TEM images of citric acid and silver after annealing (b, c).

The coating based on copper acetate (II) and polyethylene was formed with the mixture of the powders of 1:1 and 1:2 initial mass ratio of the components. The targets were obtained by thorough mixing of powders with vibrating ball mill.

The substrates were quartz plates (for spectroscopic measurements in visible area) and sodium chloride (NaCl) plates (for infrared spectroscopic measurements).

The IR spectroscopic studies were done with Fourier transform infrared (FTIR) spectrophotometer Vertex-37 (Bruker).

The spectroscopic studies were done with UV–is spectrophotometer Cary-50 (Varian). The value of the band gap (Eg) was calculated on the basis of the optical absorption spectra using linear part extrapolation of the spectral dependence on $\alpha^2 \sim f(h\nu)$ absorption coefficient square on the axis of the photon energy [4,5].

The heat treatment of the coatings was conducted during spectroscopic studies using standard thermal cycler. The heating speed was 10 °C/min. The cooling of the substrate with layers up to room temperature was done together with the thermal cycler.

The morphology of the products was characterized using the data of transmission electron microscope (TEM) JEM 2100 (Jeol). Thin layers were deposited directly onto a carbon-coated copper grid.

The elemental analysis of the formed coatings was conducted using scanning electron microscopy (SEM, Quanta 200 F) with energy-dispersive X-ray (EDX) spectrometer.

3. Results and discussion

We studied the capacity of nanoparticles based on copper to appear during the thermally initiated redox reactions in the thin-layer systems based on citric acid and metals. The citric acid acts as an oxidizer of metal thin layers and as a stabilizer of the forming nanoparticles [6]. Aluminum and copper layers deposited on citric acid coating surface intensively enter into chemical reaction with it. The result of this chemical interaction is the formation of metal salt what is confirmed by the spectroscopy IR data.

The heating of citric acid thin layer is followed by water desorption processes and its partial destruction (Fig. 2). The latter is indicated by general decline in optical density of IR spectrum absorption. When the temperature reaches 150 °C, in the spectrum appears the band near 1595 cm^{-1}. The analysis of possible chemical reactions activated by heating, allows suggesting that the appearance of this band is associated with the formation of COO— groups (antisymmetric vibrations ν_{as}(COO) [7]. The band of ν_{as}(COO) (1400–1300 cm^{-1}) symmetric vibrations is difficult to identify because of other bands presence. It is known that the absorption bands associated with the vibrations of the ionized carboxyl group appear simultaneously with disappearance of the characteristic absorption carbonyl band [7]. However, in IR spectrum of citric acid thin layer, the band near 1720 cm^{-1} does not disappear completely. It indicates that during heating the process of COO— group formation does not affect all carboxyl group of the acid.

In IR spectrum of bilayer systems based on citric acid and metal, originally there is an absorption band near 1595 cm^{-1}. It means that any additional thermal initiation is not required for chemical interaction of a thin layer of metal with citric acid. IR spectrum of citric acid–aluminum system has no noticeable differences in comparison with IR spectrum of citric acid–copper bilayer system. In electronic spectrum, the absorption associated with the surface plasmon absorption of aluminum nanoparticles, was not observed [8].

In multilayer thin-film system, including acid, copper and aluminum, in addition to salt formation process, the reactions of copper reduction from its salt can occur due to more electrochemically active metal – aluminum. In this case, can be expected the formation of nanoparticles. Therefore, the main attention was paid to the study of these ternary thin-layer systems.

After deposition, in citric acid–copper–aluminum–citric acid four-layer thin-film systems like in bilayer systems, metal layers are quickly dissolved in acid. Visually, it is accompanied by change in coating color and increase in its optical transmission. One of the

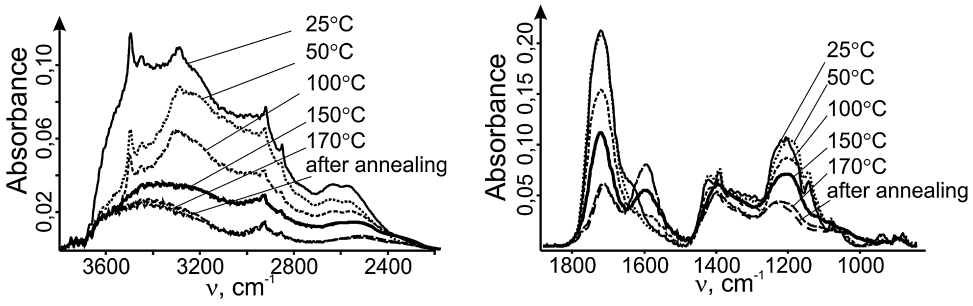

Fig. 2. FTIR spectra of thin coatings based on citric acid.