

Electrophoretic deposition of Al-CuO_x thermite materials on patterned electrodes for microenergetic applications

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Abstract. In this paper, the features and main nuances of electrophoretic deposition of energetic nanoscale powder materials based on Al and CuO_x were investigated and formulated. We have successfully demonstrated the advantage of using suspension non-stop ultrasonic mixing and horizontal electrode placement during deposition. The possibility of local deposition of energetic materials on an electrically conductive topological pattern was shown. The influence of the mass of the deposited material on the behavior of the wave combustion process of a locally formed energetic material was investigated. This study provides guidance for the multiobjective optimization and increasing the reproducibility of the local electrophoretic deposition process of energetic materials. The results indicate that Al-CuO_x mixture can be integrated into microenergy systems as a material with excellent specific energy characteristics and high combustion rate.

1 Introduction

Energy is one of the most acute and urgent areas of research in the modern World. This broad concept includes the problems of generation, conversion and storage of energy. Modern science knows a large number of ways to address these issues - from traditional to alternative. Nevertheless, it was the ability to control fire that once allowed man to take a special place among animals. Humanity has been improving its fire control skills throughout its history.

Today, researchers are looking for new ways to use the thermal energy released during self-propagating exothermic reactions between two or more components that form energetic materials, which are also called metastable intermixed composites [1-3]. The most studied of this class of materials are bimetallic systems [4,5], metal-metal oxide pairs [6] and combinations thereof [7,8]. The main parameters of the energetic material are internal energy density, amount of gas release, initiation energy, and combustion rate [9]. The Al-CuO composition has an advantageous combination of all of the above parameters, being one of the leaders among similar materials in terms of internal energy density. For example, the internal energy density for Al-CuO material is 4075 J/g, which is 4.5 times higher than that of modern lithium polymer batteries.

In addition to macro applications, these materials also find micro solutions. A large block of potential applications is associated with microenergy including microelectronics for surfaces bonding and components brazing [10], for MEMS applications [11], time delays [12, 13.], etc. Under these conditions, the development of methods for precision control of the composition and structure of the material, methods for the formation of these materials in the required areas (i.e. locally on patterned substrates) becomes a big challenge. Among other things, these methods, materials and processes must be compatible with traditional technology of integral microelectronics.

To date, commercial applications have found multilayer materials formed by layer-by-layer magnetron, electron-beam or vacuum-thermal deposition methods [14, 15]. The main disadvantage of this group of materials is the complexity of local formation, since deposition takes place over the entire area of the substrate, and also, due to the thickness of multilayer structures (up to several tens of micrometers), lithography or etching of materials becomes a very nontrivial task.

An alternative solution is the method of electrophoretic deposition (EPD), which is based on the phenomenon of the movement of charged particles under the influence of an electric field, and deposition occurs only on conductive surfaces, which removes the issue of local formation of the material. EPD is actively used to create a wide variety of devices - for medicine or electrochemical power sources [16]. In addition, in the field of energy the possibility of forming multicomponent energetic materials on the substrates surface has been repeatedly demonstrated [17-20]. EPD is a simple technique that allows the use of a variety of components, including nano-sized and nano-structured, to control material performance over a wide range.

In this work, the features of the EPD process of Al-CuO energetic materials based on nanosized powder are considered. The dependences of the material deposition rate on the applied voltage and the deposit mass on the duration of the process were determined. The possibility of local deposition of Al-CuO_x material on substrates with a topological pattern was demonstrated, and the process of its combustion was investigated.

2 Experimental details

2.1 Materials

In this work, nanopowders of Al with an average particle size of 90 - 110 nm (an oxygen content of 8–10 at. %), and CuO_x with particle average size of 50 - 80 nm were used. The CuO_x nanopowder contains CuO and Cu₂O phases, the content of other elements is not more than 0.05 wt. %. Powder materials were obtained from LLC “Advanced powder technologies” (Russia, Tomsk). Chemically pure isopropyl alcohol (99.8%) was used as a solvent.

To study the EPD features and establish dependencies the deposition process was carried out on substrates of 100 μm thick stainless steel foil. The stainless steel foil was etched in HF:HNO₃:H₂O solution (1% HF, 13% HNO₃) at a temperature of 50-60 °C for 15 minutes to remove the surface impurities. Then the substrates were washed in deionized water and dried in vapor of isopropyl alcohol. The deposition area was limited by special templates. Templates made of 1 mm plastic plates with a 12 mm round hole were placed on the substrate surface.

The second series of experiments was performed to investigate the possibility of local electrophoretic deposition. The local EPD process occurred on a sitall substrate covered with a 300 nm Ni layer. The Ni layer was formed by magnetron sputtering. To create a specific architecture of thermite material, a pattern of a nickel layer was formed using a

CNC machine with a 450 nm 15 mW laser. The pattern was made in the form of a track with rounded turns and the total length was 5 cm. The samples had “start” and “finish” pads for easy ignition and calculation of the wavefront combustion rate. Stainless steel foil was used as a counter electrode in all cases.

2.2 The methodology of EPD process

Al and CuO_x nanopowders in a mass ratio of 2:3 were used to prepare the suspension. The final total solid loading was 1 g/L. The 50 ml of suspension based on 200 mg nanopowders and isopropyl alcohol was treated with a 100 W ultrasonic homogenizer for 1 hour. Then the suspension was diluted with isopropyl alcohol to 200 ml and treated in an ultrasonic bath for 30 min. To maintain the equal conditions and the stability of the suspension the peristaltic pump system was used during the EPD process. The process was carried out in 100 ml of suspension, and the other part of the prepared suspension was treated in an ultrasonic bath. The suspension was continuously circulated through a buffer tank placed in an ultrasound bath. The temperature in the ultrasonic bath was kept no higher than 23 °C.

The process was carried out in an electrophoretic cell with a parallel horizontal arrangement of electrodes to avoid a layer thickness gradient. The distance between the electrodes was 2 cm. The process was carried out in a potentiostatic mode at electric field strength of 30 to 150 V/cm. The mass of the layer was controlled by the deposition time at a certain applied voltage.

2.3 Characterization

The deposited Al-CuO_x mass was calculated by weighing the electrodes before and after deposition. Surface morphology, thickness, and composition of Al-CuO_x layers were studied by scanning electron microscopy and energy dispersive X-ray analysis.

The velocity of combustion wavefront propagation was measured using a high-speed camera at 15000 fps. The combustion initiation in all cases was carried out using a low-power piezoelectric element. The wavefront propagation velocity is calculated from the known distance and measured time intervals.

3 Results and discussion

3.1 Features of Al-CuO_x electrophoretic deposition

As mentioned earlier in the EPD process the particles dispersed in a solvent are attracted and deposited on an electrode by applying an electric field. The electrodes are usually arranged vertically and parallel to each other. In this case, the material is deposited unevenly in thickness. In the lower layers of the suspension the concentration of the particles becomes much higher since particles tend to gradually settle down under the influence of gravity. According to Hamaker's equation (1) [21] the deposition rate w depends on the particle mobility μ , the electric field strength E , the deposition area A and the concentration of particles in solution C :

$$w = \int_{t_1}^{t_2} \mu \cdot E \cdot A \cdot C \cdot dt \quad (1)$$

As the particles move in a horizontal direction perpendicular to the electrode at different speeds depending on the concentration in a certain suspension layer, the deposit is formed rather thicker in the lower part of the sample. In works [22, 23] authors confirm the fact of uneven deposition when the electrodes are arranged vertically.

For microenergy purposes the thermite material must combust evenly, so keeping the same thickness over the entire area is very important. The layer is formed more homogeneously during deposition with horizontally arranged electrodes because the particles move against the gravity. In addition, the movement of large particles and agglomerates up towards the electrode is also hampered by gravity. As a result the formed layer has a lower amount of agglomerates. However, using only a horizontal cell does not completely eliminate the influence of the particle concentration gradient in the suspension on deposit uniformity and process reproducibility. The other nuances should be taken into account:

1. The concentration of suspended particles decreases over time by gravity and this affects the adsorption rate of the material on the electrode (regardless of the location of the electrodes)
2. Total nanopowder loading of suspension decreases as the particles adsorb onto the electrode, which is also affects the deposition rate
3. Electrophoretic mobility of heterogeneous components differs and accordingly, the stoichiometry of the suspension changes as the particles adsorb onto the electrode.

Therefore, it can be concluded that all particles must be suspended in the suspension throughout the entire process and total nanopowder loading must be high relative to the average deposit mass per process. However, obtaining a highly stable suspension is not a trivial task. Additives such as surfactants are often used to increase the electrostatic stabilization of particles, but the presence of additional components in the deposited material can also affect its properties. In this work stabilizing additives were not used. For stabilization and nonstop suspension circulation through the ultrasound bath the peristaltic pump system was used. Also, we used a large volume of the suspension of 200 ml with a 200 mg loading to minimize the change in the material deposition rate on the substrate from the particle concentration in the suspension. Therefore, the suspension concentration did not change much from the original concentration after several successive EPD processes, since the samples were formed with a deposit mass of no more than 4 mg.

This section presents the results of particle deposition to the horizontally located electrode at non-stop suspension mixing. **Fig. 1.** shows the dependence of the deposited layer mass on the applied field strength to the cell for 2 and 4 minutes deposition process.

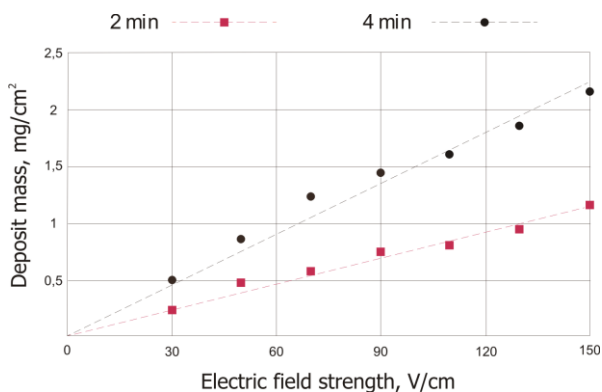


Fig. 1. Dependence of the deposited layer mass on the applied potential to the cell

To plot the dependence, the samples were prepared by successive EPD processes at electric field strengths from 30 to 150 V/cm from the one prepared suspension. The process was carried out at certain EPD process times: 2 and 4 minutes. The graph shows that the electrophoretic deposition rate changes linearly with increasing applied voltage. The dependence trend is maintained when the deposition process time is increased to 4 minutes. In previous work [24], an experiment was performed to establish similar dependence. The difference was that a smaller volume of suspension was used and the suspension was not mixed nonstop. In that work, a deviation from linear dependence after 100 V/cm was detected. However, in that case, the true effect of electric field strengths on the deposition rate cannot be estimated since the suspension was partially settled and the suspension was quickly depleted due to the small nanopowder loading (50 mg). These results confirm the effectiveness of using a large suspension volume and non-stop suspension circulation for high process reproducibility.

The highest material deposition rate on the electrode is observed at 150 V/cm. It would seem that a high deposition rate is the most efficient because less time is spent on the process. However, there may be a larger number of agglomerates in the adsorbed layer and the elements may be unevenly distributed among each other when the deposition process occurs at high electric field strength. Therefore, an average electric field of 70 V/cm was chosen as optimal. **Fig. 2.** shows the elements mapping of the sample deposited at 70 V/cm.

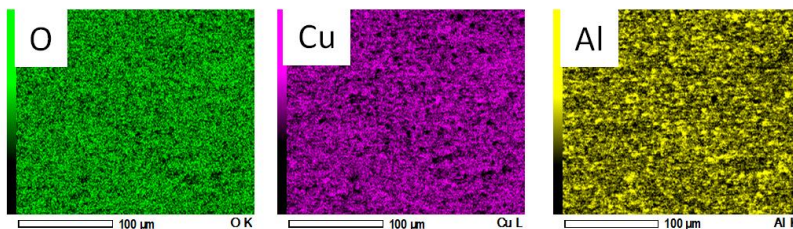


Fig. 2. The elements distribution map on the surface of Al-CuO_x sample deposited at 70 V/cm

The element distribution map shows that the elements are evenly mixed. The elemental analysis showed that the layer contains 30 wt.% CuO_x. Earlier in the work [24] dependence of the deposit composition on the CuO_x content in the original suspension for a similar total loading of 1 g/L was established. It was shown that from a suspension with the same stoichiometry nanopowder content a layer with 22 wt.% CuO_x content was deposited. The difference of 8 percent can be explained by the fact that in this work the suspension volume is twice as large and there was also non-stop suspension mixing using the pump system.

After establishing the optimal process mode, it is necessary to plot the dependence for control the mass or thickness of the deposited layer. Since mass of the thermite material actively affects the combustion characteristics. In the EPD process the Al-CuO_x mass can be regulated by the deposition time. **Fig. 3.** shows the dependence of the deposited layer mass on electrophoretic deposition time and SEM image of a deposited Al-CuO_x layer with a mass of 1 mg/cm² (3 min deposition).

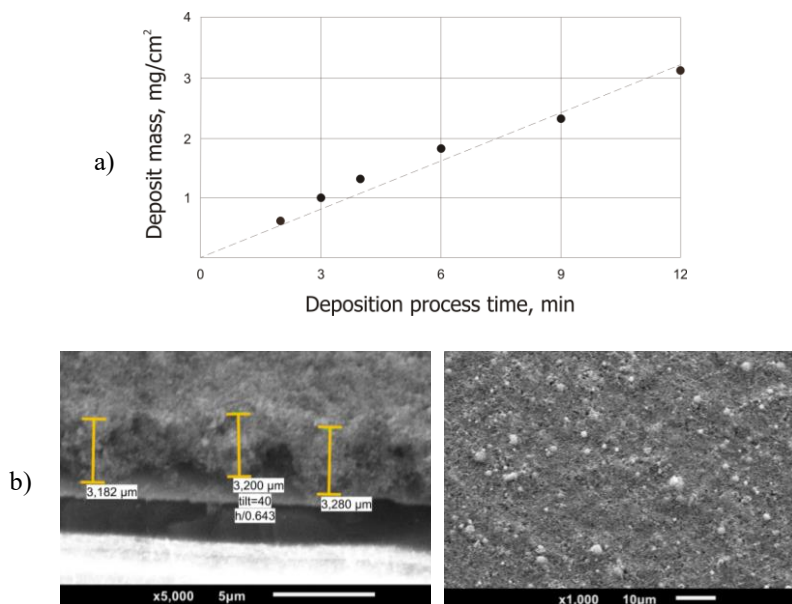


Fig. 3. a) The Dependence of the Al-CuO_x deposited layer mass on the deposition time b) SEM images of 3 min deposited sample

The graph shows that the dependence is linear in the given time interval. The layer thickness at a 1 mg/cm² Al-CuO_x mass is approximately 5 μm. The SEM image of the layer surface shows large aluminum particles, these particles are initially contained in the original nanopowder in small amounts. The image does not show large pores and microcracks, indicating that the layer is sufficiently dense and uniform.

3.2 Investigation of combustion wavefront propagation

In this section, the possibility of local deposition and the features of the wavefront propagation of the Al-CuO_x deposited material are investigated. Samples with different masses of Al-CuO_x deposited on a sitall plate with a nickel track were produced. Sitall was chosen as a substrate because it has a low thermal conductivity and allows the reduction of dissipation of heat released as a result of a high-exothermic thermite reaction. The deposition process time to achieve the required mass was chosen based on the graph of **Fig. 3. a)**. **Fig. 4** shows a combustion process of the Al-CuO_x material with a 1, 2, 3 mg/cm² mass deposited at 70 V/cm.

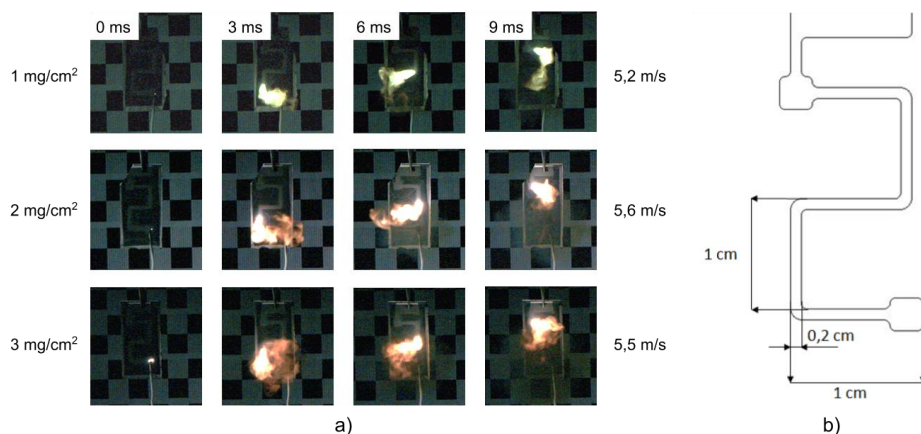


Fig. 4. a) The storyboard of the Al-CuO_x material combustion process, b) the scheme of nickel track on sital plate

The analysis of the combustion process showed that the wavefront propagates at the same speed in all sections of the track. The wavefront propagation velocity of 1, 2 and 3 mg/cm² samples was 5,2, 5,6 and 5,5 m/s respectively. Increase in Al-CuO_x mass does not significantly enhance wavefront propagation velocity, but noticeably increases gas generation. In theory, the wavefront propagation velocity should increase with increasing mass of the thermite layer, but a slight decrease has been noticed. It is possible that the sample with the higher mass has morphological differences. Perhaps the sample with the highest mass has morphological differences. The main assumption is that microcracks are formed on a sample with a high layer mass after solvent evaporation. In the paper [25], the authors noted that the number of cracks increases with increasing mass of the electrophoretically deposited layer. Cracks may affect the combustion performance. In the presence of microcracks, the contact between the components decreases, which leads to a thermite reaction slowdown. Also, microcracks can act as gas-release vents, thus reducing the impulse of the reaction flow. The work [26] presents the results of a combustion characteristic study of Al-CuO_x layers printed on a 3D printer in the form of structures with vents for a gas outlet. It has been found that the wavefront propagation velocity decreases with increasing vent size.

4 Conclusions

In this work, factors that increase the stability of the EPD process were considered. Non-stop mixing by a peristaltic pump system and large volume of suspension are beneficial for efficiency and reproducibility of the EPD process. The electric field strength of 70 V/cm was chosen as optimal for the formation of a high-quality and uniform Al-CuO_x layer. The possibility of forming the specific architecture of thermite material with a certain mass and composition by the EPD process is shown. Combustion characteristics can be controlled by changing the mass of the thermite layer. The minimum combustion velocity of the Al-CuO_x layer was 5,2 m/s, and the maximum was 5,6 m/s. The combustion process analysis of deposited layers showed that the wavefront propagates uniformly at the same speed. The developed technique of Al-CuO_x electrophoretic deposition can be successfully used to create a material with a high combustion velocity, low initiation energy, and different specific architecture.

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