

High temperature synthesis of copper coatings made from a thin film layered composition "CuO -B - Glass"

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Abstract. The study is aimed at developing methods for producing thin-layer cermet coatings. Such coatings are promising for use in flat heating elements, thermal protective coatings. A method for producing electrically conductive coatings based on copper and borosilicate glass using the technology of self-propagating high-temperature synthesis is proposed. The wave synthesis and thermal explosion in the CuO – B – glass thin-layer system were studied using experimental methods and developed mathematical models. The effect of the reaction layer thickness and inert additive on the kinetics of the process and characteristics of final products was studied. Numerical calculations were performed to study the dynamics of the process. The thermophysical and kinetic parameters that determine the synthesis in the CuO – B – glass system are found using the inverse method.

Introduction

Synthesis of thin-film layered compositions is an important task of modern materials science [1, 2]. At present, thin-film systems are widely used in optical waveguides, neutron mirrors, microelectromechanical systems (MEMS), for creating protective coatings and as heating elements [3, 4]. Such heaters are usually obtained using a mixture of electrically conductive powder with glass. During heat treatment, glass melts and binds powder particles, ensuring electrical contact between them [5]. As a rule, for this process the temperatures of 800–1000 °C are needed, which complicates the method and requires expensive and energy-consuming high-temperature furnaces. Using the advantages of self-propagating high-temperature synthesis (SHS), high temperatures can be obtained at low energy consumption [6].

The essence of the method is that a suspension of a mixture of reactive powders in isopropyl alcohol is applied to the ceramic or metal substrate by screen printing. After the mixture dries, an exothermic reaction is initiated, during which a coating is formed containing the target phases, for example NiAl, Ti₂AlC [7-14]. A similar method allows the preparation of coatings of various compositions and does not require the use of high-temperature furnaces.

In this work, we propose a method for producing copper conductive coatings, which are obtained by reduction a powder of copper oxide with boron.

The aim of the work was to study the formation of copper coatings during SHS in thin layers of the CuO – B – glass powder system using experimental methods and macroscopic mathematical models.

Experiments

The powders of copper oxide of high purity (CuO, TU 6-09-02-391-85), brown boron and inert boron lead glass (PbO-SiO₂-B₂O₃) were used in the experiments. The initial sample contained a thin powder



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layer ($\text{CuO} + \text{B} + \text{glass}$, or without glass) placed on a ceramic plate. The $3\text{CuO} + 2\text{B} \rightarrow 3\text{Cu} + \text{B}_2\text{O}_3$ synthesis reaction was conducted in two modes: combustion and thermal explosion.

In order to initiate a synthesis wave, a spiral connected to the laboratory transformer was connected to the sample. A TCA thermocouple was fixed in the middle of the sample. The signal from TCA thermocouple was supplied to the input of an analog-to-digital converter (ADC).

The velocity of the combustion front was determined by the time of the combustion front propagation over a sample at a certain distance that was measured with an accuracy of 1 mm, and the propagation time was recorded using a stopwatch with an accuracy of 0.01 sec.

For conducting synthesis under thermal explosion, the initial sample was placed in a tube furnace. A TCA thermocouple was in direct contact with the sample. A voltage of 70–120 V across the furnace was set applying the laboratory transformer, and the ADC was used for data acquisition. After occurrence of temperature perturbation, the recording of data continued for 1–2 min, and then the ADC and the furnace were turned off.

The microstructure of the synthesized sample was investigated using an Axiovert 200M MAT microscope. The phase composition of the synthesis products was determined with a portable tabletop X-ray device (RIKOR, Cok_α radiation) at the Tomsk Common Use Center SB RAS. Differential thermal analysis of the initial mixture was performed with a NETZCH STA 409 PC/PG derivatograph in air at a heating rate of 10 deg/min. The electrical resistance of the samples was measured using an F-410 ohmmeter (measurement range of $1 \cdot 10^{-2} \div 1 \cdot 10^7$ Ohm).

Discussion of experimental results

To study the processes occurring in the reaction mixture, differential thermal analysis of a stoichiometric CuO-B mixture was performed at a heating rate of 10 deg/min in air. Differential thermal analysis is presented in figure 1.

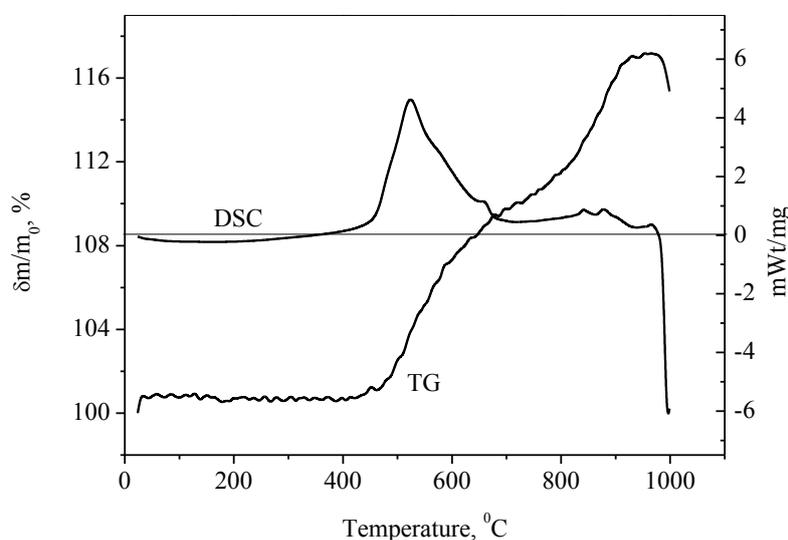


Figure 1 Differential thermal analysis of a stoichiometric mixture.

The analysis shows that the process develops in stages with an increase in mass in the temperature ranges of 450–700 °C and 750–950 °C. Moreover, a significant exoeffect that consists of several peaks is observed in the first temperature range. Two small exoeffects are observed in the second temperature range. In the range of 950–1100 °C, there is a loss of mass accompanied by endoeffect. Thus, the main heat release in the reaction mixture can be expected when heating to a temperature above 450 °C. Thermodynamic analysis of the mixture showed that the adiabatic reaction temperature was about 2955 °C. However, endoeffect in the range of 950–1100 °C, probably related to evaporation or decomposition of reaction products, will restrict the maximum reaction temperature.

The composition of the products produced during isothermal air annealing of the samples to which a glass powder was added (figure 2a) was studied using X-ray diffraction.

X-ray diffraction shows that when the samples are heated to the initiation reaction temperature, the mixture consists only of copper oxide CuO and a small amount of Cu₂O. As the temperature of heat treatment increases, the reflection intensity of the CuO phase gradually decreases and the reflection intensity of Cu₂O increases. Moreover, the relative content of Cu₂O calculated from the reflection intensity becomes maximal at 750 °C (figure 2b). The content of the Cu phase increases almost linearly, and the phase of metallic copper becomes predominant at 900 °C. This change in the content of reaction mixture components is typical for the processes proceeding gradually with the formation of intermediate products.

That is, it can be assumed that reduction develops in stages according to the following formula: CuO → Cu₂O → Cu. After the process is completed, the sample represents a copper coating consisting of copper drops melted together with each other. The surface of the drops is completely or partially covered with a layer of Cu₂O formed due to the oxidation of the copper surface with atmospheric oxygen. The fact that the particles are melted together with each other is confirmed by high electrical conductivity of the coating (electrical resistance of the sample is less than 1 Ohm).

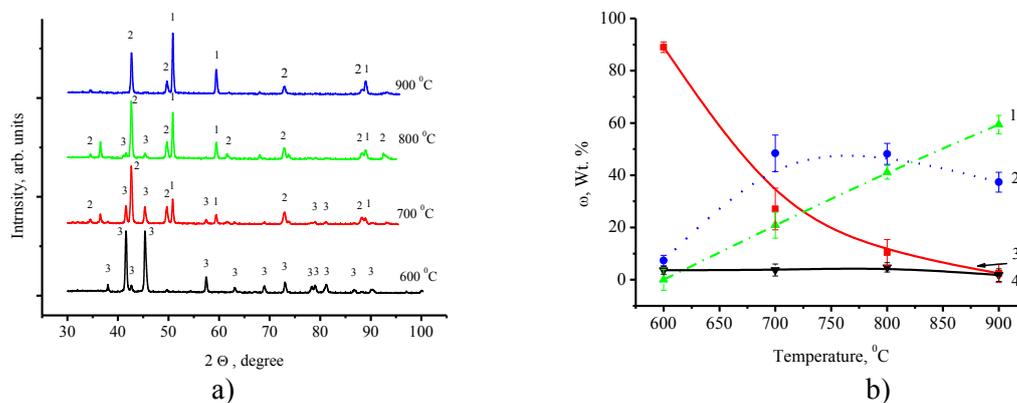


Figure 2 X-ray diffraction patterns (a) and the content of phases (b) in the samples heat-treated at different temperatures. Phases are denoted as: 1 – Cu, 2 – Cu₂O, 3 – CuO, 4 – Cu₄O₃.

The method of visual observation confirmed that the propagation of combustion wave consists of a series of flashes which occur one by one and resembles a relay mechanism. The velocity of the reaction front was studied depending on the layer thickness of the initial mixture (figure 3).

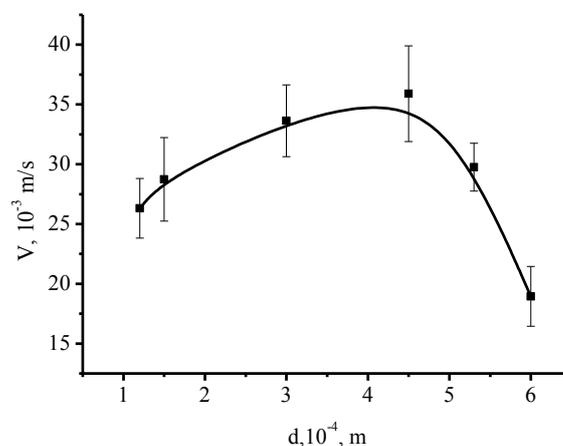


Figure 3. Velocity of the combustion front versus the layer thickness

This dependence has a maximum. It was found that the front does not move when the layer thickness is less than $1 \cdot 10^{-4}$ m: the combustion wave either stops or moves in an unstable mode; the reaction develops only in certain areas; the continuous front is absent. When the layer thickness is more than $4 \cdot 10^{-4}$ m, the front is continuous, and its velocity increases with increasing a layer thickness.

The effect of the layer thickness on the thermogram demonstrating the synthesis of the CuO - B - glass system in the thermal explosion mode is given in figure 4, a. It was shown that the duration of synthesis increased and the maximum temperature significantly decreased at a relatively small thickness of the reaction layer, apparently due to large heat losses.

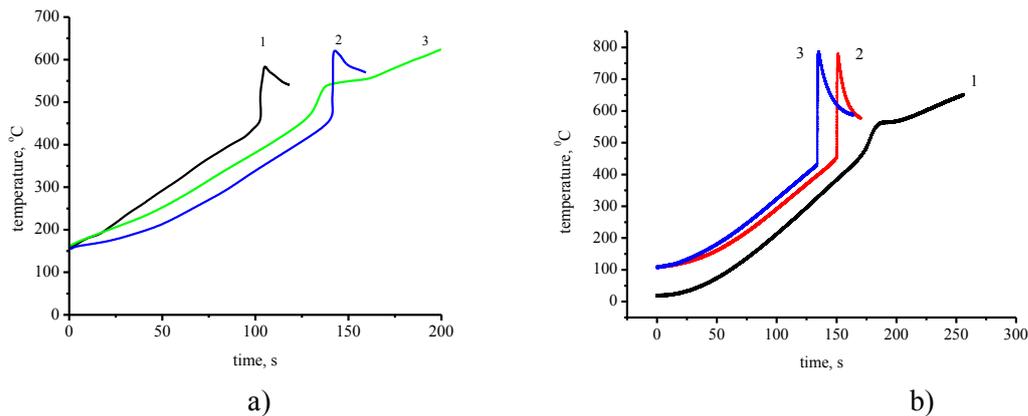


Figure 4. Thermograms of the process depending on the layer thickness of the initial mixture: (a) 1 - $3.4 \cdot 10^{-4}$, 2 - $5.1 \cdot 10^{-4}$ and 3 - $9.2 \cdot 10^{-4}$ m, and when glass is added to the initial mixture (b). Mass fraction of glass in the mixture: (1) 50, (2) 33, (3) 66 wt.%.

With increasing the thickness of the coating, when heat loss is neutralized due to the exoeffect of chemical transformations, the maximum synthesis temperature increases sharply and remains almost constant. The increase in the amount of inert additive (glass) in the reaction layer leads to the decrease in the thermal effect of chemical reaction, and when the content of the inert additive is 60 wt.%, the synthesis is conducted under soft conditions, with sufficiently low self-heating (figure 4, b). In the latter case, uniform copper coatings with good electrical conductivity are formed.

Mathematical model

A sample prepared from stoichiometric powders of CuO and B which form the product $3\text{Cu} + \text{B}_2\text{O}_3$ during a single-stage chemical reaction with or without the addition of an inert additive I (glass) is considered. The difference in the density and heat capacity of the initial mixture and product is not taken into account. The sample is placed in a furnace with a temperature of T_p . The processes are mathematically modeled in a macroscopic approximation.

The equation for the rate of chemical transformation of the initial mixture into the reaction product is given in the form

$$\frac{\partial \alpha}{\partial t} = f(\alpha) k_0 \exp\left(-\frac{E}{RT}\right) \quad (1)$$

t is time; T is temperature; α is the chemical transformation degree determined as the mass fraction of the product in the reaction mixture; R is the universal gas constant; k_0 is a pre-exponential factor; E is the activation energy of chemical reaction; $f(\alpha)$ is a kinetic law. To simplify further calculations and obtain analytical relations, it is assumed that $f(\alpha) = 1$.

Two limiting modes of synthesis are considered: wave and volume (thermal explosion).

Wave synthesis. The heat conductivity equation in a thin-layer reaction sample, neglecting the nonuniform distribution of temperature over its thickness and with allowance for possible melting of the very low-melting component (Cu) formed during synthesis, is given by

$$[c_p - c_{Cu}L_{Cu}\delta(T - T_{L,Cu})\alpha]\rho \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \rho(1 - m_I)[Q + c_{Cu}L_{Cu}e(T - T_{L,Cu})] \frac{\partial \alpha}{\partial t} - \frac{\chi}{d}(T - T_n) \quad (2)$$

x is the spatial coordinate; c_p , ρ , λ are the heat capacity, density and thermal conductivity of the initial mixture; c_{Cu} is the mass concentration of Cu in the final reaction product; m_I is the relative mass of inert material in the initial mixture; Q is the thermal effect of reaction; χ is the effective heat transfer coefficient of the reaction layer with the environment, d is the thickness of the reaction layer; $T_{L,Cu}$, L_{Cu} are the temperature and heat of melting of Cu ;

$$\delta(T - T_{L,Cu}) = \begin{cases} 0, T \neq T_{L,Cu} \\ \infty, T = T_{L,Cu} \end{cases} \text{ - Dirac delta function; } e(T - T_{L,Cu}) = \begin{cases} 0, T < T_{L,Cu} \\ 1, T \geq T_{L,Cu} \end{cases} \text{ - Heaviside function.}$$

The initial and boundary conditions can be written as follows.

$$t=0: T(x) = T_n, \alpha(x) = 0; \quad (3)$$

$$x=0: T = T_w (t < t_w), \frac{\partial T}{\partial x} = 0 (t \geq t_w); \quad x = +\infty: T = T_n \quad (4)$$

In (3), (4) T_w , t_w are the temperature of the heated wall ($T_w > T_n$) and the time of its contact with the sample.

Thermal explosion. The equation of energy conservation in the sample, neglecting the temperature distribution over the volume of the substance ($Bi \ll 1$), in the adiabatic approximation is given as follows

$$[c_p - c_{Cu}L_{Cu}\delta(T - T_{L,Cu})\alpha]\rho \frac{\partial T}{\partial t} = \rho(1 - m_I)[Q + c_{Cu}L_{Cu}e(T - T_{L,Cu})] \frac{\partial \alpha}{\partial t} + W \quad (5)$$

$W = \frac{\chi}{d}(T_n - T)$ is the rate of heat transfer of the sample with the external environment. It is also

assumed that the temperature of the furnace in which the reaction sample is placed varies linearly $T_n = T_H + \Omega t$, T_H is initial temperature, $\Omega \equiv const$.

Initial conditions are set as

$$t=0: T = T_H, \alpha = 0. \quad (6)$$

The mathematical model (1) - (4) was used to study numerically wave synthesis. The heat conductivity equation was solved using an implicit difference scheme and the sweep method. For thermal explosion, the system of equations (1), (5) with the initial condition (6) was calculated according to the first order Euler scheme. In the calculations, the reduced values of the initial parameters were taken from the works in [15, 16]. In addition to this, thermal and thermokinetic parameters were obtained using the inverse method: $Q = 2.5 \cdot 10^5$ J/kg, $E = 184000$ J/mol, $k_0 = 10^{10}$ 1/s, $\chi = 62$ J/(m²·K·s). The dependence of the average velocity of the combustion front propagating over a thin-film sample is shown in figure 5. It is seen that with an increase in the thickness of the reaction sample the flame rate increases, reaching a limit value corresponding to the parameters of combustion under adiabatic conditions.

As can be seen in figure 5, the theoretical dependence $\bar{v}(d)$, in contrast to the experimental one (figure 2), does not have a maximum due to the above assumptions in the mathematical model. At the same time, numerical calculation is in good agreement with experimental data.

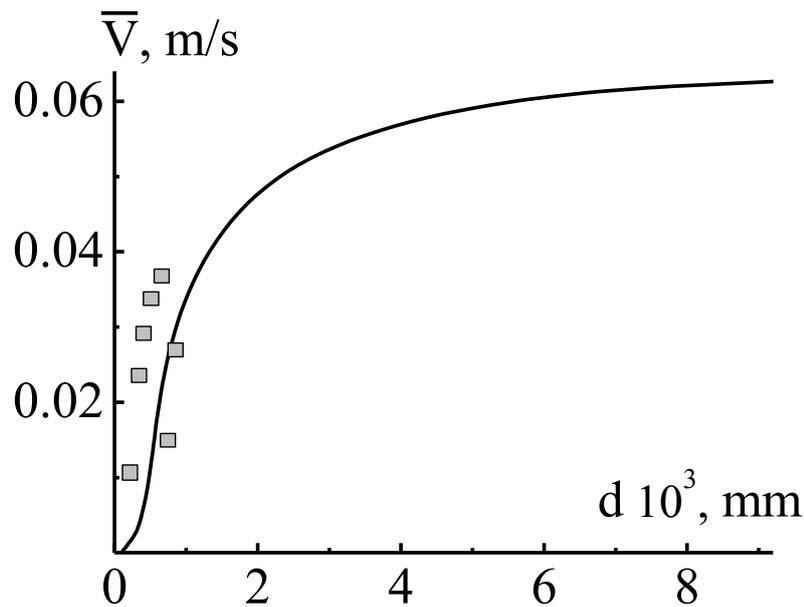


Figure 5. Average combustion rate of the sample versus the thickness of the reaction layer. The solid line is the calculation, the square is the experiment.

Figure 6 shows that a decrease in the thickness of the reaction layer due to the stronger effect of the heat removal on the dynamics of synthesis leads to less heating required for the occurrence of thermal explosion (a). Addition of an inert component to the reaction sample contributes to an increase in the duration of synthesis and the ignition temperature of the mixture (b). At the same time, the presence of glass in the mixture reduces the thermal effect of chemical reaction and, ultimately, leads to a decrease in the maximum synthesis temperature.

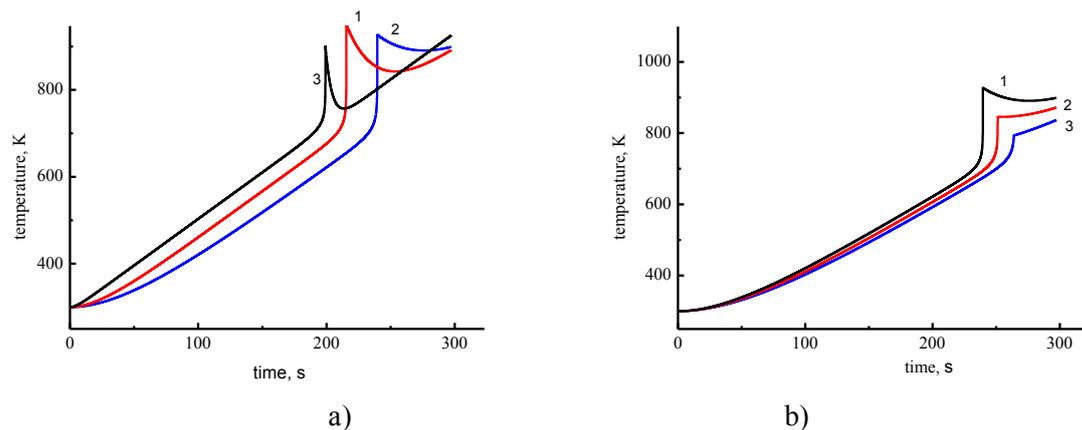


Figure 6. Dynamics of the thermal explosion temperature in the CuO - B - glass system: (a) for $m_i = 0.3$ and different values of the reaction layer thickness $d = 10^{-3}$, m: 1 - 1, 2 - 0.5, 3 - 0.1; (b) for $d = 10^{-3}$ and the different amount of additives: 1 - 0.3, 2 - 0.5, 3 - 0.7.

As shown in Figs. 5 and 6, the theoretical dependences are in good agreement with the experimental results.

Conclusions

1. Synthesis of the Cu-B-glass thin-layer system was experimentally studied. Physical and chemical processes in the system develop in several stages with the formation of metallic copper as final products and the Cu_2O , Cu_3O_4 oxides as intermediate products. Combustion was found to occur in the multifocal mode, and the front velocity depends on the thickness of the reaction layer according to a parabolic law with a maximum at a layer thickness of $4 \cdot 10^{-4}$ m.

2. Macroscopic mathematical models were developed for wave synthesis and thermal explosion in the thin layer Cu – B – glass system. Dynamics of the process was numerically calculated. Theoretical estimates were in good agreement with experimental data. The thermophysical and thermokinetic constants of the process were determined by the inverse method.

Notifications

SHS - self-propagating high-temperature synthesis;

MEMS - microelectromechanical systems;

ADC - analogy to digital converter;

TCA - chromel-alumel thermocouple.

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