Production of ceramic materials based on the system of Co–Cr–O, Ce–O by the method of SHS

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Abstract. The regularities of the processes occurring during the thermal decomposition of cobalt, chromium, cerium and sucrose nitrates were studied. Nanodimensional oxide ceramic materials based on oxides of cobalt, chromium, cerium, CoCr₂O₄ are obtained. The effect of the composition of the initial mixture, the mass of the sample, and the rate of heating on the formation of the synthesis product, its phase composition was established. It is shown that the process can proceed in the autoignition mode. A sample was prepared containing the catalytic layer on a porous metal-ceramic support. The obtained sample has catalytic activity in the afterburning process of exhaust gases.

1. Introduction
Nanodisperse powders based on oxides of cobalt, chromium, cerium are used as pigments, cathode materials of electrochemical current sources, catalysts for various organic reactions [1]. Traditional methods of synthesis of such materials – solid–phase or sol–gel–synthesis have a number of disadvantages. At present, the method of “combustion of solutions” is more promising. This method is simple, has low energy costs, has no by-products or industrial waste. This method produced many different compounds, mainly oxide ones. However, this method can also be used to obtain nanoscale powders of metals, for example, nickel [2]. The difference between this method and the traditional sol–gel or ceramic is as follows. It is known that salts of many metals, especially in higher oxidation states, are strong oxidants. However, the thermal decomposition process is endothermic. The process can be converted to exothermic by adding a reducing agent, or “fuel”. Due to the oxidation of these compounds, the necessary temperature for the decomposition of salt is formed. Many organic compounds are used as a “fuel”, for example, glycine [3, 4].

Despite the extensive literature on the production of nanopowders by the sol–gel combustion method, for example [5-9], there are few data on the regularities and mechanisms of the combustion process. There is no exact data on what causes the ignition temperature in such a system. The mechanism of structural transformations is unknown: sol–gel → solid particle. The main parameters of the combustion wave, their influence on the properties of the synthesis product, and the methods of controlling the process have been little studied. This makes it important to study such systems.

This work is devoted to the study of the regularities of the processes occurring during the thermal decomposition of cobalt, chromium and cerium nitrates in the presence of sucrose serving as a reducing agent. The choice of these salts is due to the fact that the oxides of cobalt, chromium, cerium and also cobalt-chromium spinel formed during the reaction are active catalysts for afterburning of automobile exhaust gases. Sucrose is chosen as a “fuel” because it is a good reducing agent. In
addition, sucrose increases the viscosity of aqueous salt solutions, which increases the thickness of the applied layer and the efficiency of the catalyst.

The aim of the work is to study the regularities of processes occurring in the SHS process of nanoscale oxide ceramic materials based on the Co–Cr–O, Ce–O system and the study of their functional properties.

2. Procedure
To aqueous solutions of cobalt nitrate, chromium, or their equimolar mixture as well as cerium nitrate (0.4 mol / l), sucrose was added as a reducing agent and dried at a temperature of no higher than 40° C. The gel obtained as a powder was used as precursor for synthesis. To study the thermal decomposition of precursors, a gel-like powder weighing 0.5-3 g was placed in a crucible. The crucible was installed in an electric furnace, which was powered by an alternating voltage of 100-150 V from the autotransformer. By adjusting the voltage, the temperature was increased at a constant rate. The thermocouple was placed directly in the gel. The thermocouple is connected to the USB ADC LA20 and a personal computer. In addition, the temperature was controlled by a second thermocouple located on the inner wall of the furnace.

Coatings on a porous cermet were obtained by repeatedly immersing it in a precursor solution with intermediate drying at 100-150°C and final firing in air at 350-700°C. The phase composition of the synthesis products was determined on a portable desktop X–ray instrument RIKOR, (radiation CuKα) provided by Tomsk Common Use Center SB RAS.

3. Discussion
Figure 1a shows thermograms of the decomposition of cobalt, chromium nitrates and their equimolar mixture. On the thermograms, the curve is seen to be inflected corresponding to the physico–chemical transformations taking place in the sample. It can be seen that thermal decomposition of cobalt and chromium nitrates is consistent with data obtained by differential thermal analysis [10]. The decomposition of chromium nitrate proceeds as follows: at 50-60°C there is a phase transition – the melting of the salt in its own crystallization water. A solution of salt in water forms. With a further increase in temperature to 130–160°C, salt hydrolysis and evaporation of water proceed. Oxynitrates of the composition are formed: Cr(OH)2 × 3Cr(NO3)3 × xH2O, Co(OH)2 × 2Co(NO3)2 × xH2O. In addition, partial oxidation of the ions to Co3+ and Cr6+ occurs. At a temperature of 200–250°C, a solid product is formed on the basis of non-stoichiometric cobalt oxide or chromium oxide. In the future, Cr2O3 and CoO or Co3O4 are formed, respectively. Thermal decomposition of a mixture of nitrates proceeds similarly, however, the temperature of the last stage - the formation of oxides is much lower.

![Figure 1. Thermograms of decomposition of cobalt nitrates (curve 1), chromium (curve 2) and their equimolar mixture (curve 3) (a) as well as mixtures of cobalt nitrate with sucrose (curve 1) and equimolar mixture of cobalt and chromium nitrates with sucrose (curve 2) (b).](image-url)
In fact, it corresponds to the hydrolysis temperature of the initial salts. Probably, the formation of a solid product occurs as a result of the combined hydrolysis of cobalt and chromium nitrates and subsequent dehydration. The thermal decomposition of salts in the presence of sucrose proceeds differently. In figure 1b it can be seen that at 50–100°C an endothermic effect is observed corresponding to the formation of an aqueous solution of salts and sucrose. And at 130–160°C, an exothermic effect is observed, during which, probably, oxidation of sucrose and formation of a solid product takes place.

In figure 2a shows the thermograms of a mixture of cobalt and chromium nitrates and sucrose with a different content of sucrose in the mixture. It can be seen that the temperature of the thermal effects and their intensity depend on the content of sucrose in the mixture. The highest intensity of effects is observed with a sucrose content of 30 wt.%. Probably, this quantity is sufficient for oxidation–reduction reactions to proceed. The influence of the sample mass on the formation of the reaction product was also studied (figure 2b). It can be seen that the increase in the mass of the sample is accompanied by an increase in the duration of the processes at a temperature of about 50°C. This is explained by the fact that an increase in the amount of the substance required to form salt solutions requires a longer time.

It has been established that processes in a mixture of cobalt, chromium and sucrose nitrates can occur in the autoignition regime (figure 3). In this case, self–ignition begins at a temperature of 150°C. This temperature corresponds to the oxidation temperature of sucrose. The maximum temperature reaches 600°C and above. This is sufficient to form a solid product. In figure 4 shows the thermograms of the synthesis product heat–treated at a temperature of 800°C. It is seen that when the content of sucrose in the starting mixture is 30 and 50 wt. % cobalt–chromium spinel of CoCr2O4 composition is formed. With a sucrose content of 70 wt. %, a phase other than CoCr2O4 is formed. The interpretation of the diffractogram with help at the moment does not allow to identify this connection.

Based on the studies carried out, a method has been developed for depositing a catalytic layer on a porous cermet support [11]. To this end, a suspension was prepared containing an aqueous solution of cobalt, chromium, cerium nitrate and also finely dispersed alumina. The carrier was immersed in the resulting suspension, dried at 150°C and calcined at 350°C. The process was repeated 3–5 times. As a result, a porous layer containing alumina, cerium and cobalt chromium spinel was obtained on the surface of the support. The resulting sample is tested as a catalyst for afterburning exhaust gases and allows a 10% reduction in CO and NOx in exhaust gases.

**Figure 2.** Thermograms of the decomposition of an equimolar mixture of cobalt and chromium nitrates with sucrose. The content of sucrose 30 (curve 1), 50 (curve 2), and 70 wt. % curve 3) (a) mass of sample 1 (curve 1) 1.5 (curve 2), 2 (curve 4) and 3 grams (curve 3).
4. Conclusions
1. The regularities of the processes occurring in the SHS process of nanoscale oxide ceramic materials based on the Co–Cr–O, Ce–O system were studied.
2. The effect of the composition of the initial mixture, the mass of the sample and the rate of heating on the formation of the product of synthesis, its phase composition was established.
3. It is shown that the process can proceed in the autoignition regime.
4. A sample was prepared containing the catalytic layer on a porous metal-ceramic support. The obtained sample has catalytic activity in the afterburning process of exhaust gases.

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