Self-propagating high-temperature synthesis of oxide bronzes with regulated composition and properties

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Abstract. The work is devoted to the preparation of oxide tungsten bronzes of various compositions and various structures by the SHS method. The work is aimed at the realization of the ability to control the composition, structure and properties of SHS products. Brightness pyrometry technique was used for the experimental evaluation of the temperature in the combustion wave. The values of the electrical conductivity of the obtained samples of oxide tungsten bronzes with constant current: for K₀.25WO₃ — 0,029 S/cm; K₀.50WO₃ — 0,046 S/cm. Carbon paste electrode was produced and tested based on an oxide bronze K₀.50WO₃.

1. Introduction

Oxide bronzes of transition metals represent interstitial solid solution of general formula М¹, М²Оₙ, where М¹ are atoms of alkaline or other strongly electropositive metals, М² = Ti, Mo, W, Re, Ru, V, Nb, Ta, Pt, 0 < x < 1, the value of n is determined by the degree of oxidation of the element М². Most of the oxide bronzes have distorted structure of the prototype, i.e. the oxide of the transition metal. The alkali metal atoms are located in voids or channels structure formed by linking octahedra М²О₆ through vertices, edges, faces [1].

Peculiarities of crystal and electronic structure of oxide bronzes generate a large variety of their chemical, electrical, and optical properties. In particular, they are characterized by mixed ionic-electronic conductivity [2]. These compounds have been successfully used as components of various functional inorganic materials. This electrode materials [3-5], corrosion-resistant coating [6], materials for laser medicine [7,8], efficient catalysts [9,10]. As a rule, changing the structural characteristics leads to a change in the physical and chemical properties of the oxide bronzes, which offer a challenge for practical application.

Potassium tungsten oxide bronze depending on the content of potassium atoms crystallize in several structural types, hexagonal and tetragonal symmetry (Table 1) [11]. Formation of three-dimensional scaffold structures is typical for all tungsten bronzes by connecting the octahedra WO₆ vertexs. The potassium atoms statistically occupy the positions of the widest parts of the channels of the structure [12].

Methods and conditions of synthesis of oxide bronzes like for many non-stoichiometric compounds largely determine their composition, and hence structure and properties. It is known, in particular, the increase in the values of conductivity and even change the type of conductivity of the oxide bronzes with the increase in the concentration of embedded atoms alkali metal [13,14].

One of the modern methods of research of physical and chemical processes regulating the composition and purity of the SHS products is a method of brightness pyrometry. High-speed thermal
imaging systems can record the dynamics of the temperature field on the sample surface. An experimental study of the combustion front at the microlevel using a high-speed camera described in the papers [15-18].

Table 1. Crystallographic data concerning KₓWO₃

| Chemical formula | Space group | Symmetry | Z  | Cell parameters, Å |
|------------------|-------------|----------|----|-------------------|
| K₀.₂₀WO₃         | P 6₃22      |          | 6  | a = 7.389         |
|                  |             |          |    | c = 7.510         |
| K₀.₂₅WO₃         | P 6₃22      | hexagonal| 6  | a = 7.3991        |
|                  |             |          |    | c = 7.649         |
| K₀.₂₆WO₃         | P 6₃        |          | 6  | A = 7.389         |
|                  |             |          |    | c = 7.508         |
| K₀.₃₃WO₃         | P 6₃/mcm    | hexagonal| 6  | A = 7.384         |
|                  |             |          |    | c = 7.501         |
| K₀.₄₈WO₃         | P 4/mbm     |          | 10 | a = 12.285        |
|                  |             |          |    | c = 3.833         |
| K₀.₅₇WO₃         | P 4/mbm     | tetragonal| 10 | a = 12.260        |
|                  |             |          |    | c = 3.826         |

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This work is devoted to preparation of oxide tungsten bronzes of different composition and different structure SHS method. The work is aimed at the realization of the ability to control the composition, structure and properties of SHS products by changing the content in the charge of exothermic additive, which determines the adiabatic temperature of the process. Brightness pyrometry technique was used for the experimental evaluation of the temperature in the combustion wave.

2. Experimental

2.1. Synthesis

Self-propagating high-temperature synthesis (SHS) was carried out according to the reaction

\[ 2\text{CuO}\cdot\text{WO}_3\cdot\text{W}+2\text{KI} \rightarrow 2\text{K}_x\text{WO}_3+2\text{Cu}+2\text{I}_2, \]

where KI is used as a reducing agent.

The molar ratio of the components of the charge is shown in the Table 2. The total mass of the mixture was about 2 g. The mixture was thoroughly ground into a homogeneous mass in an agate mortar. Tablets having a diameter of 1.5 cm were prepared; ethanol was used as the binder. The process was initiated by the heated tungsten spiral. Purification of the synthesis products from metallic copper and iodine was carried out with concentrated nitric acid and ethanol.

The mixture CuO+W was as an exothermic additive in the absence of which the reaction in SHS mode is impossible. In excess of exothermic additive, the reaction proceeded with the explosion.

Calculation of temperature of combustion was carried out in the adiabatic approximation, which allowed to estimate the maximum temperature achieved during synthesis. The results of the calculation of the enthalpy of reaction and adiabatic temperatures of the combustion process SHS of the potassium tungsten bronzes listed in the Table 2.
Table 2. The composition of the charge mixture and combustion products

| No | The composition of the charge mixture (molar ratio) | ΔH_{298}, kJ/mol | T_{ad}, K | The resulting products according to XRD |
|----|--------------------------------------------------|------------------|----------|----------------------------------------|
| 1  | WO_3 : KI                                        | +2.5             | —        | No reaction                            |
| 2  | 3CuO : W : WO_3 : KI                             | -1580            | 1400     | K_{0.25}WO_3, WO_3                     |
| 3  | 6CuO : 2W : WO_3 : KI                             | -2650            | 2000     | K_{0.50}WO_3, WO_3                     |
| 4  | 9CuO : 3W : WO_3 : KI                             | -2900            | 2400     | Explosion                              |

X-ray powder diffraction was used to identify products as well as to characterize their structure. Experiments were performed on a Philips X'Pert Pro diffractometer using Cu Kα-radiation.

Quantitative determination of potassium was performed to clarify the composition formulae of the compounds with atomic absorption spectrometer AA240Z Varian.

2.2. Thermal-imaging
We used the system of optical checking of parameters of the combustion process SHS [15]. General characteristics of the registration process:
- sampling resolution — 5.85 μm;
- timing resolution — 1 ms;
- picture size — 500×1280 pix.

As the temperature model a tungsten lamp TRU 1100-2350 with the known dependence of the brightness temperature on the current flowing through its spiral has been used.

2.3. Conductivity measurement
The specific conductivity of the oxide bronzes were determined in pressed tablets (P =20 MPa) by four- and two-probe methods. Compact features: \( r = 1 \text{ cm} \), \( h = 0.5 \text{ cm} \), \( \rho = 3.84 \text{ g/cm}^3 \), the average size of the crystallites ~200 nm.

2.4. Preparation of carbon paste electrode and potentiometric measurements
Carbon paste electrode was made of fluoroplastic rod with diameter 4 mm, length 50 mm with a small air hole on the butt. The air hole is filled with a mixture of spectrally pure graphite and the oxide bronze K_{0.50}WO_3. The average particle size of the used substances was ~200 nm. Paraffin was used as a binder. The ratio of the components graphite: K_{0.50}WO_3:paraffin = 10:1:1. The surface area of the working part of the electrode was 0.25 cm². Platinum wire served as a contact. The reference electrode was a saturated silver chloride electrode. Buffer mixture was used as electrolytes in a wide interval of pH values (2.0-12.0).

The particle size was controlled with laser diffraction on the device LA-300 Horiba.

3. Results and Discussion
SHS for non-organic substances takes place under extremely high temperatures and may be accompanied by explosion, so the calculation of the thermodynamic parameters of the synthesis, including an estimate of the adiabatic temperature is a very important and usually preceding the experiment.

By varying the proportion of the exothermic additive, we actually assigned the adiabatic temperature of the process. The greater amount of exothermic additive (CuO+W) in the sample contributed to greater degree of conversion reaction and the synthesis of products with a high content of potassium (K_{0.25}WO_3 and K_{0.50}WO_3 respectively).

Figures 1 and 2 show the X-ray diffraction patterns of K_xWO_3 obtained by the SHS method with different amounts of exothermic additives.
Figure 1. X-ray powder diffraction pattern (selected range) of the resulting product (● — the main phase K$_{0.25}$WO$_3$; ■ — an admixture of WO$_3$).

Figure 2. X-ray powder diffraction pattern (selected range) of the resulting product (● — the main phase K$_{0.50}$WO$_3$; ■ — an admixture of WO$_3$).

Using high-speed video recording and computer data processing (camera “VideoSprint”) of the SHS process allowed to describe the temperature distribution in the sample volume. The time, brightness temperature and the coordinates of the corresponding point of the sample were recorded in the combustion process at the same time. The result is a video sequence by which it was possible to determine the boundaries of the reaction zone. The maximum temperature recorded in each zone was taken as the adiabatic temperature process.

Figure 3. The distribution temperature in the volume of the sample (composition of charge No.3, Table 2)
The temperature instability is due to some heterogeneity of the composition and dispersion of the charge, which, in turn, lead to uneven heat transfer through the model. Experimentally obtained values of temperatures are a good approximation to the calculated values (Table 2).

Table 3 shows the measured values of specific conductivity of the samples of the obtained oxide bronzes at permanent current.

| Chemical formula | Specific conductivity, S/cm |
|------------------|-----------------------------|
| $K_{0.25}WO_3$   | 0.029                       |
| $K_{0.50}WO_3$   | 0.046                       |

The obtained results are coherent with the literature data on the conductivity of oxide bronzes of other compositions [19,20]. Increasing values of conductivity is quite logical with increasing the content of potassium, because the electrons in potassium provide the conductive properties, getting themselves to the conduction band [21].

Since the oxide bronze tungsten atoms are formally in at least two different oxidation states, they should behave in solution as oxidation-reduction systems the potential of which is determined by the activities of the oxidized and reduced forms and the activity of hydrogen ions

$$K_xWO_3 + 2H^+ + 2\overline{e} \rightarrow K_{x-1}WO_3 + H_2O.$$  

Having a good electrical conductivity, it is unnecessary to implement indifferent electrode in a system for the registration of potential. In other words, the oxide bronzes should function as hydrogen or glass electrodes. High resistance of bronzes to acids and alkalis creates preconditions for maintaining the hydrogen functions in a wide range of pH. The change of electrode potential in solutions of different acidity (pH 2.0-12.0) shown on the diagram (figure 4). Potential of carbon paste electrode in a solution with a certain pH value was established after 5-10 min.

![Figure 4](image1.png)  
**Figure 4.** The dependence of the EMF system $K_{0.50}WO_3$–silver chloride electrode on pH.

![Figure 5](image2.png)  
**Figure 5.** Potentiometric titration 0.1 mol/l HCl by 0.1 mol/l NaOH solution with carbon paste electrode based on $K_{0.50}WO_3$.

We carried out quantitative potentiometric determination of hydrogen chloride in the hydrochloric acid solution by the method “added-found” (figure 5) with the use of a carbon paste electrode of the indicator as the indicator (the reference electrode is saturated silver chloride electrode). Experimentally obtained data well coincided with the theoretical.

4. Conclusions

So by varying the contents of exothermic additive in the charge and thereby assigning the adiabatic temperature of the synthesis process, we were able to obtain an oxide bronze of different composition:
K_{0.25}WO_3 and K_{0.50}WO_3. These bronzes belong to different structural types, they greatly differ in properties, in particular, they have different electrical conductivity.

The use of optical monitoring systems of parameters of the combustion process has allowed to experimentally assess the temperature, developing in the process of synthesis. We recorded a higher adiabatic temperature during the synthesis with a high content of exothermic additive (CuO + W).

We have shown the possibility of using the obtained oxide bronzes as electrode materials. It was suggested in earlier literature that oxide bronzes of transition metals can be used as indicator electrodes in potentiometric oxidation-reduction and acid-base titration [22]. Carbon paste electrode, that we have made, based on bronze K_{0.50}WO_3 was applied as indicator electrode in potentiometric acid-base titration and showed quite satisfactory performance.

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