Mathematical modeling of combustion wave propagating in SH-synthesis of functional borides used to protect from mixed ionizing radiation

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Abstract. This work describes the mathematical model of SHS combustion wave propagating in the system of W-B. The model is based on the heat equation. The result of modelling is a forecast of SH-synthesis temperature regime in this system what allows forecasting a phase composition and thermal stresses. The model checking was realized in the experiment in the synthesis of this system in a laboratory-scale plant including the SHS reactor. The presented model is in agreement with the experiment in a maximum synthesis temperature and the curve rate of synthesis carrying out.

1. Introduction

The nuclear power using is closely associated with ionizing radiation which is observed throughout all stages of nuclear fuel cycle. Ionizing radiation is divided into four types:

- heavy particles with a positive charge: fission products and α-particles;
- light charged particles: electrons and positrons;
- gamma radiation: photons with different energy;
- neutron radiation: thermal, resonance and fast neutrons [1].

Shields minimizing radiation intensity are used as the most effective equipment protecting from ionizing radiation. The first two types of ionizing radiation have a short mean path in every condensed media, so that the problem of protecting from these particles is generally not considered. On the contrary, gamma and neutron radiation has long mean paths practically in all matters. A shield materials selection depends on projectile particles type, so materials containing chemical elements with large atomic number, such as lead, tungsten and different steels are used to protect from photons. In order to protect from neutron radiation hydrogen-containing mediums are applied: water, polyethylene, paraffin wax and others. Elements highly absorbing neutrons, such as boron and cadmium, also can be used [2].

Generally neutron radiation is accompanied by gamma radiation, so that combinations of different materials or composites are used to protect from these radiation types. One of these materials is tungsten boride (WB). A tungsten presence in a compound allows using this material to protect from gamma radiation while a boron presence allows protecting from neutron one. Furthermore, this compound has the high density which is approximately equal to 16 g/cm^3. This feature has a positive influence on its protecting properties [3].

Tungsten borides are obtained by direct synthesis from elements, carbothermal reduction of metal and boron oxides, borothermal reduction of metal oxides [4]. However the most advanced material engineering technology for WB obtaining is the method of self-propagating high-temperature synthesis (SHS) [5].

The SH-synthesis is a technology based on the ability of some chemical elements and compounds to undergo exothermic reactions.

The SHS consists of following stages:

– heat is added pointwise to a product consisting of reagents mixture;

– a reagents thin layer is heated and undergoes an exothermic reaction;

– the next sample layer is heated to synthesis temperature imitation due to thermal conductivity, after that reagents undergo the chemical exothermic reaction;

– a reaction wave propagates over whole sample.

The synthesis scheme is presented in figure 1.

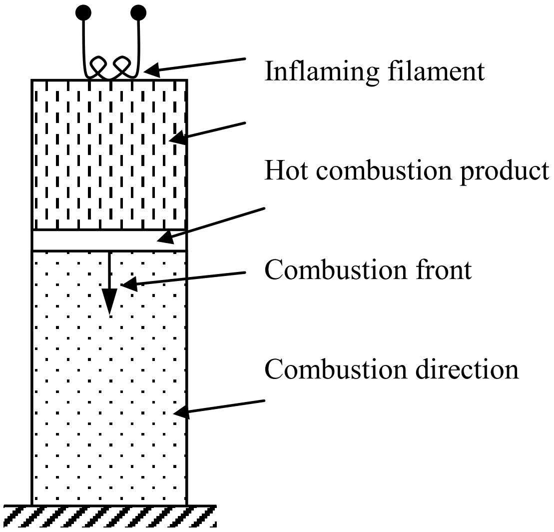

Figure 1. SHS process scheme.

The batch preparation conditions, such as powders extrusion pressure, ratio of initial reagents amount, sample pre-heating and others, have a great influence on finished product properties during the synthesis. Specifically, a mathematical modeling necessity of combustion wave propagating in SH-synthesis process appears to forecast obtained materials properties.

2. Experimental

A mathematical modeling of SHS process is an extremely difficult problem whereas it is necessary to take into account macroscopic, mesoscopic and microscopic scales [6]. The most of parameters are averaged to simplify mathematical models. A model is considered as solid, although it is porous in reality.

The simplest mathematical models of SH-synthesis carrying out are based on the heat equation [7]:

$$c \cdot \rho \cdot \frac{\partial u}{\partial t} = \lambda \cdot \Delta u + f(\vec{r}, u, \eta), \tag{1}$$

where c – sample specific heat capacity;
ρ – sample density;
u – temperature;
λ – sample thermal conductivity coefficient;

$f(\vec{r},u,\eta)$ – heat sources function;
$\vec{r}$ – position;
t – time;
η – mass fraction of chemical reaction product.

Specific heat capacity, density, thermal conductivity coefficient, heat sources function and mass fraction of chemical reaction product are functions of position, time and temperature in the general case. The temperature depends on time and position.

The heat sources function depends on different parameters. This function can be divided to several parts to simplify it [7]:

$$f(\vec{r},u,\eta)=Q\cdot\rho\cdot k(u)\cdot\varphi(\eta), \tag{2}$$

where Q – specific standard heat of formation; $k(u)$ – temperature activation function; $\varphi(\eta)$ – kinetic function of chemical reaction behavior.

These functions also depend on position, time and temperature.

The temperature activation function represents the Arrhenius equation for a chemical reaction rate:

$$k(u)=k_0\cdot\sqrt{u}\cdot e^{-\frac{E_a}{R\cdot u}}, \tag{3}$$

where k_0 – pre-exponential factor; E_a – chemical reaction activation energy; R – Boltzmann constant.

The kinetic function can be presented as a combination of rather simple functions:

$$\varphi(\eta)=e^{-m_s\cdot\eta}\cdot\eta^{-n_s}\cdot(1-\eta)^{n_c}, \tag{4}$$

where m_s – drag parameter; n_s – drag parameter; n_c – chemical reaction order.

M_s, n_s and n_c coefficients depend on reagents types. Typically an exponential law is carried out during the SH-synthesis, in other words $m_s \neq 0$, $n_s = n_c = 0$.

The mass fraction change of chemical reaction product can be found using the following differential equation:

$$\frac{d\eta}{dt}=k(u)\cdot\varphi(\eta). \tag{5}$$

Let us consider a two-dimensional case in a cylindrical coordinate system. So, the equation (1) becomes the following:

$$c\cdot\rho\cdot\frac{\partial u}{\partial t}=\lambda\cdot\left(\frac{\partial^2 u}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial u}{\partial r}+\frac{\partial^2 u}{\partial z^2}\right)+f(r,z,u,\eta), \tag{6}$$

where r – position length; z – height.

Within the framework of studies the SHS is carried out in vacuum, so that a heat transfer from sample borders is probable only with the help of radiation. A sample bottom is thermal insulated. According to [8], the boundary condition for sample top and bottom, consequently, is as follows:

$$\lambda\cdot\left.\frac{\partial u}{\partial z}\right|_{z=H}=-\varepsilon\cdot\sigma_B\cdot\left(u^4-u_e^4\right);\quad \lambda\cdot\left.\frac{\partial u}{\partial z}\right|_{z=0}=0, \tag{7}$$

where H – sample height; u_e – environment temperature; ε – emissivity factor; σ_B – постоянная Stefan-Boltzmann constant.

The boundary condition for the side boundary is similar to the boundary condition for the sample top:

$$\lambda \cdot \left.\frac{\partial u}{\partial r}\right|_{r=R} = -\varepsilon \cdot \sigma_B \cdot \left(u^4 - u_e^4\right), \tag{8}$$

where R – sample radius.

Let us assume that the sample at the initial time was heated uniformly, so mathematically it is as follows:

$$u\big|_{t=0} = \text{const} = u_0 , \tag{9}$$

where u_0 – initial temperature of heated sample.

The product mass fraction is equal to 0 because initially a reagents mixture is under lower temperature, than a reaction initiation temperature, so mathematically it is as follows:

$$\eta\big|_{t=0} = 0. \tag{10}$$

The thermal and physical properties of initial mixture can be found in a simplified form by the following way:

$$c_0 = c_1 \cdot \eta_1 + c_2\left(1-\eta_1\right); \quad \lambda_0 = \lambda_1 \cdot \eta_1 + \lambda_2\left(1-\eta_1\right), \tag{11}$$

where $c_{0,\,1,\,2}$ – specific heat capacity of initial reagents mixture, the first reagent and the second reagent; $\lambda_{0,\,1\,,2}$ – thermal conductivity coefficient of initial reagents mixture, the first reagent and the second reagent; η_1 – mass fraction of the first reagent in an initial reagents.

The thermal and physical properties of the whole mixture can be defined by the following correlations:

$$c = c_f \cdot \eta + c_0\left(1-\eta\right), \quad \tilde{\lambda} = \lambda_f \cdot \eta + \lambda_0\left(1-\eta\right), \tag{12}$$

where c_f – specific heat capacity of synthesized substance; λ_f – thermal conductivity coefficient of synthesized substance; $\tilde{\lambda}$ – sample thermal conductivity coefficient excluding its density changing.

If a sample density is lower than maximum theoretical density there are pin holes in it. A pin holes presence in the sample has a great influence on its thermal conductivity coefficient. The thermal conductivity of gases is approximately equal to 10^{-1} W/(m·K) that is by two orders lower than the thermal conductivity of solids. So, let us assume that pin holes are filled with a gas non-conducting the heat, in other words let us set the thermal conductivity of gases in the pin holes to 0. Consequently, the sample thermal conductivity is equal to:

$$\lambda = \tilde{\lambda} \cdot \frac{\rho}{\rho_0}, \tag{13}$$

where ρ_0 – maximum theoretical density of initial reagents mixture.

In order to simplify the model let us accept that the synthesis process is carried out by one following chemical reaction:

$$\mathrm{W} + \mathrm{B} \rightarrow \mathrm{WB} + Q. \tag{14}$$

The index 1 will be understood as B, the index 2 will be understood as W, the index f will be understood as a synthesized product WB.

The heat capacity values of elementary substances, for instance of B and W and synthesized WB, were taken from [9, 10]. The temperature dependence of heat capacity is presented there by the following polynomial:

$$c_{1,\,2}=\frac{4.1868}{\mu_{1,\,2}}\cdot\left(\alpha_{1,\,2}+10^{-3}\cdot\beta_{1,\,2}\cdot u+10^{5}\cdot\gamma_{1,\,2}\cdot u^{-2}\right). \tag{15}$$

where $\mu_{1,\,2\,f}$ – molar mass of substances with indexes 1, 2, *f*; *α*, *β*, $\gamma_{1,\,2,\,f}$ – constant quantities for substances with indexes 1, 2, *f* (Table 1).

Table 1. Thermal and physical constants.

Parameter	B (1)	W (2)	WB (*f*)
α	1.54	5.74	13.89
β, K^{-1}	4.4	0.76	-0.78
γ, K^{2}	0	0	-5.02
μ, kg/mol	10.82	183.84	194.66
λ, W/(m·K)	1.5	100	30
ΔH, J/mol	0	0	$-71.128\cdot10^{3}$

It is known that a thermal conductivity of most substances at high temperatures weakly depends on temperature. A thermal conductivity rapidly changes only during phase transitions. However, let us neglect a thermal conductivity as a function of temperature because phase transitions are not considered in this model. The thermal conductivity coefficients of B, W and WB were used according to the sources [3, 10, 11] for the temperature of 1500 K (Table 1) because a synthesis initiation starts approximately at this temperature.

The standard formation enthalpy of WB is presented in [12]. Using this quantity the following quantity can be calculated:

$$Q=\frac{-\Delta H\cdot\rho}{\mu_f}, \tag{16}$$

where ΔH– standard formation enthalpy of a substance.

The environment temperature and the sample initial temperature were set equal to:

$$u_e=303\text{ K};\quad u_0=1023\text{ K}. \tag{17}$$

In order to verify the model experiments in the synthesis of this compound were carried out using the reaction (14). The SH-synthesis of tungsten boride consists of several stages. In the early stage an initial reagents powder mixing is carried out in the cubic mixer AR 403 All-Purpose Equipment. Then a batch pressing is carried out using the hydraulic press P338. The sample preparation parameters are presented in table 2. Batches were prepared on the basis of the exothermic reaction (14).

Table 2. Batch preparation parameters.

Parameter	System of W-B
Powder grades	B-99A; PTT
Mixing time, min	30
Extrusion pressure, MPa	16
Pressing duration, min	15
Billet diameter, mm	30
Billet height, mm	10-20

The SH-synthesis of material was initiated after pressing by the local heat supply. The synthesis was carried out in technical vacuum on the test bed for pyrometric research of SH-synthesis process including a SHS-reactor. The SHS-reactor is presented in figure 2.

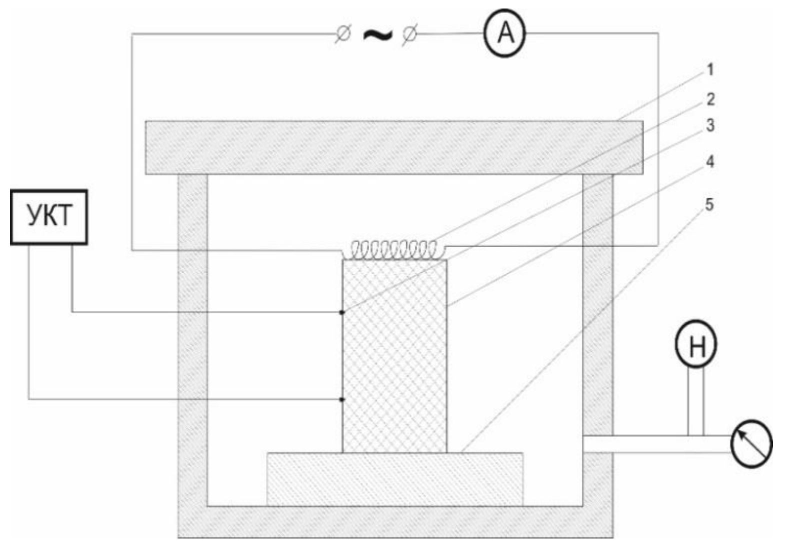

Figure 2. Experimental facility for SHS-materials obtaining: 1 – reactor head; 2 – tungsten filament; 3 – thermocouple complex; 4 – synthesized sample; 5 – nonflammable platform.

3. Results and Discussion

The synthesis process was controlled by tungsten-rhenium thermocouple complex. The temperature regime of synthesis behavior and the mathematical modeling results are presented in figure 3.

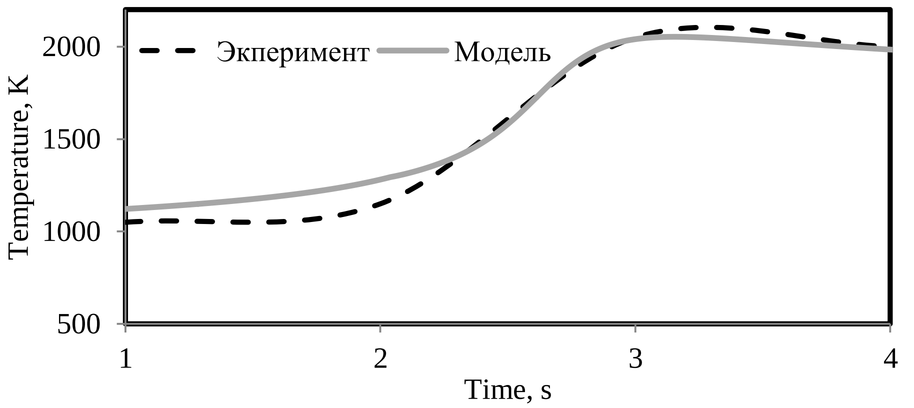

Figure 3. Synthesis temperature regime.

Figure 3 shows that both the model and the real SHS process match in the maximum synthesis temperature, the curve rate of synthesis carrying out and in the sample cooling-down. However, the violent reaction is observed not so clearly in the experiment resulting in the more long-time sample heating. It is connected with phase transitions or chemical reactions which are different to the reaction (14).

After the SH-synthesis realization the obtained materials were X-ray phase analyzed in the diffractometer Shimadzu XRD-7000 with CuK α-radiation. The analysis results are presented in figure 4. The phase composition analysis was carried out using the data base PDF 4+, as well as the full-profile analysis program POWDERCELL 2.5.

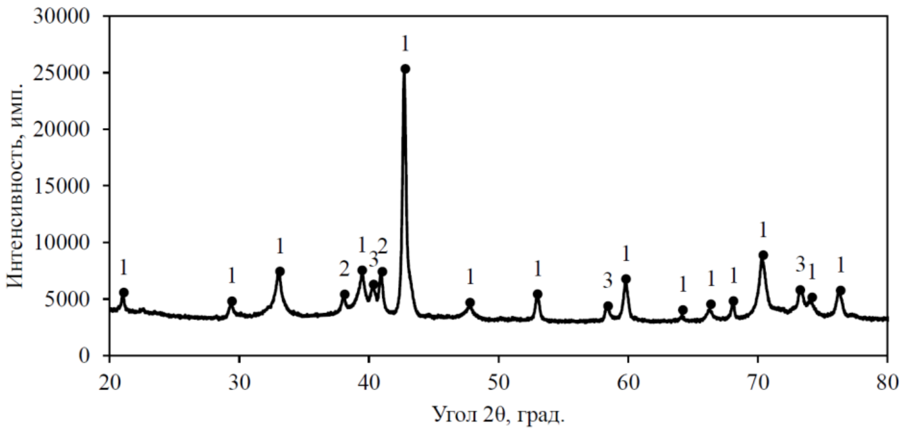

Figure 4. Synthesized substance roentgenogram:
1: WB – 82 %; 2: WB_2 – 10 %; 3: W – 8 %.

4. Conclusion

This work presents the research of W-B system reaction mechanism during the SHS. The SHS of this system combustion was mathematically modeled on the basis of heat equation. The heat source function represented the combination of specific standard formation heat, temperature activation function (according to Arrhenius equation) and kinetic function of reaction behavior. The result of this model is a forecast of synthesis temperature regime in the W-B system which allows forecasting a sample phase composition and thermal stresses. In order to verify this model the SH-synthesis of this system was carried out in technical vacuum (what is in agreement with the model boundary conditions) controlling temperature by tungsten-rhenium thermocouple complex. Following on from the obtained results it may be concluded that both the model and the real SHS process match in the maximum synthesis temperature (2000 K), the curve rate of synthesis carrying out and in the sample cooling-down. The mistiming of sample heating both in the experiment and in the model may be removed by taking into account phase transitions and WB_2 formation reaction.

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