# SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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## 1.Introduction

Self-propagating high-temperature synthesis (SHS) - the process of moving wave chemical reaction by the reagent mixture to form a solid end product, conducted with the aim of synthesis of compounds of materials. CBC mode is a strong flow of exothermic reaction (combustion reaction) in which localized heat generation in the bed and is passed from layer to layer by heat. (Shown in Figure 1)

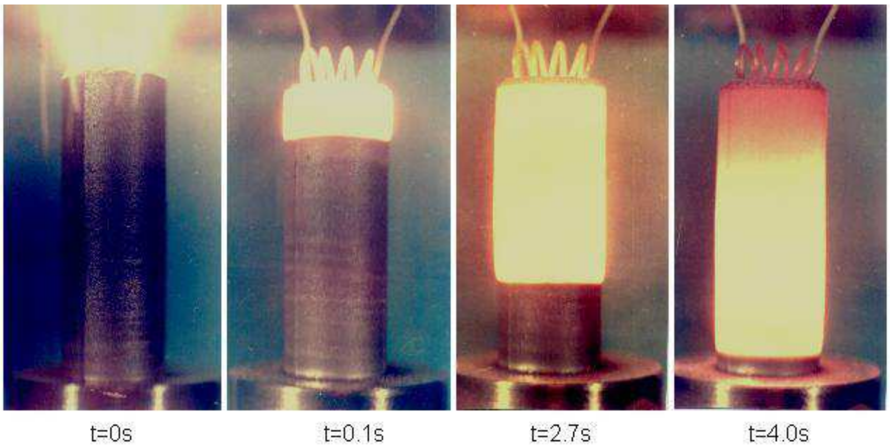


Fig.1

The aim of the work was to study ways to control the SHS process for the example of a lanthanum-boron.

## 2.Source Systems

### 2.1.Morphology of reagents and types of source systems

Reagents used in the SHS process to form fine powders, thin films, liquids and gases. The most common type of two systems: the mixture of powders (or a compacted bulk density), and hybrid systems dioxide powder (or pressed agglomerate). SVS-known processes and systems: powder-liquid gazovzves, film-film, gas-gas.

The main requirements for the initial system - providing conditions for effective interaction of the reactants.

Batch processes in SHS can be in vacuo, outdoors, or reacting, in an inert gas under pressure.

### 2.2.Chemical classes of components of the original systems

In creating the SAF system may involve all the reactive substances at high temperatures, the reactants (chemicals, individual compounds multiphase structure) and inert substances as fillers or diluents.

Most Popular reagents:

$H_2$, B, Al, C, $N_2$, $O_2$, Mg, Ti, Nb, Mo, Si, Ni, Fe, $B_2O_3$, $TiO_2$, $Cr_2O_3$, $MoO_3$, $Fe_2O_3$, NiO, etc.

As reagents used as industrial minerals and waste.

Terms matching components SHS system:

- exothermic interaction of reactants
- Cumulative formation of solids

- technical and economic feasibility.

### 3.Processes

### 3 .1.Combustion in SHS processes, it was called "solid flame" (or "solid-" burning)

The three most common types of combustion:

- gasless (Mixed combustion in engines without outgassing or release of small amounts of impurity gas)
- filtration (burning-in hybrid systems with the filter inlet reactant gas to the combustion front)
- multiphase (combustion in multiphase media - the source or generated)

### 3 .2.Initiation methods

The main way - local initiation of the reaction on the surface of the system by supplying short heat pulse (electric coil, spark discharge, laser beam, etc.) to form a combustion wave and its distribution is not heated to the starting material. The duration is typically much less than the initiation time of the combustion charge.

In some cases (eg, for weakly exothermic reactions), the process is initiated by heating the entire surface of the charge in the furnace and carried it out in a thermal explosion(Fig. 2)

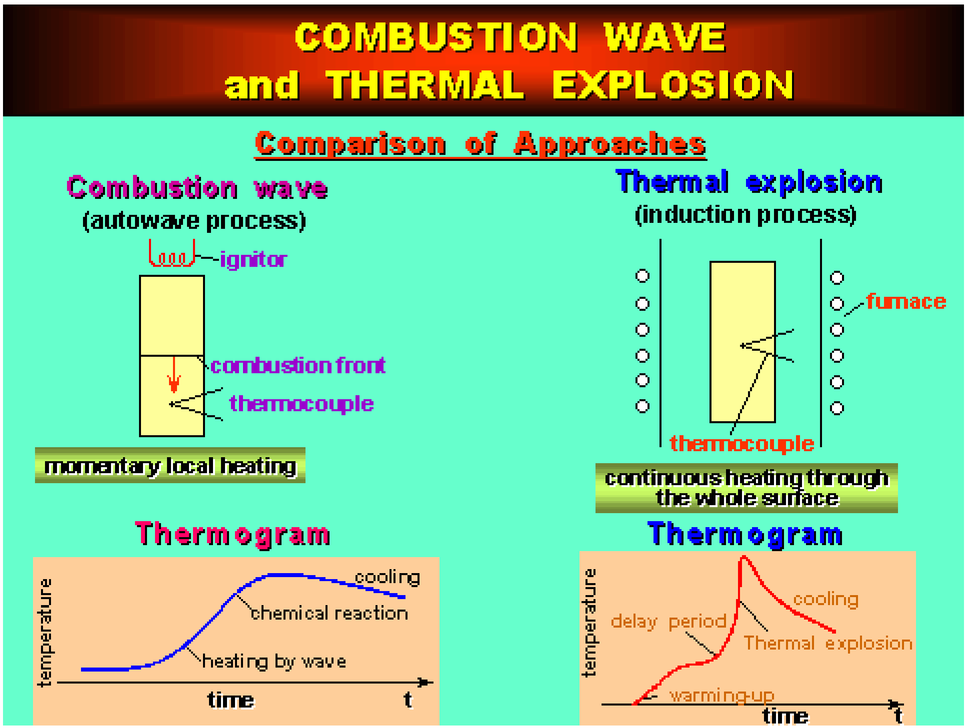


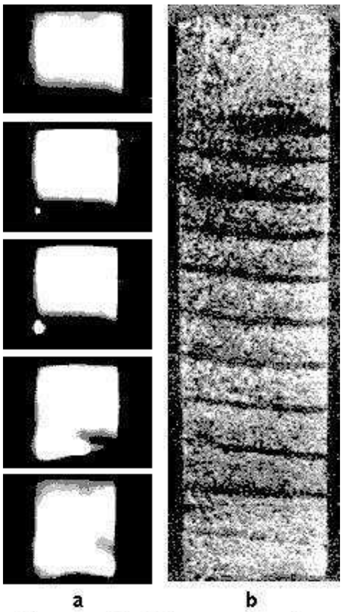
Fig.2

### 3.3.Regimes of propagation of the combustion front

In the simplest and most important steady state (Fig. 3) all points of the front move at a constant in time and the same speed. When stationary regime loses its stability, can be unstable regimes of front propagation:

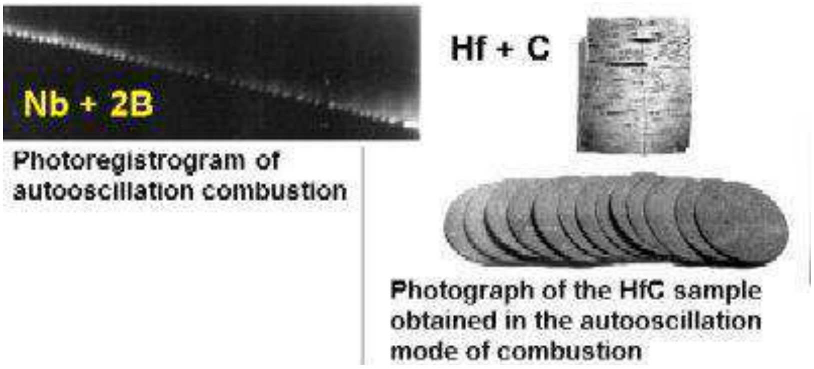
- flat rate oscillations of the combustion front ( pulsating combustion (Fig. 4)),
- localization of the combustion reaction in the centers moving along a helical path ( spin waves (Fig. 5)),
- random motion set combustion sources (solid chaotic flames).

Combustion wave is not covered by the charge in the case of strong heat loss to the environment (small diameters of charge samples, low adiabatic reaction temperature of reagents).



Frames of spining combustion of hafnium in nitrogen (a) and photograph of the end product (b)

Fig. 3 gure 5



Photoregistrogram of autooscillation combustion

Photograph of the HfC sample obtained in the autooscillation mode of combustion

Fig. 4

### 3 .4.Thermogram burning

Thermogram burning - this temperature dependence of the charge at a fixed point of time for clash of the combustion wave. simplest thermogram (Fig. 6) consists of the ascending portion, with the point of maximum temperature (combustion temperature) and downstream area (cooling). On more complex thermograms are kinks, kinks, plateaus (isothermal surface). In unstable combustion regimes in the thermograms recorded temperature fluctuations on the ascending phase.

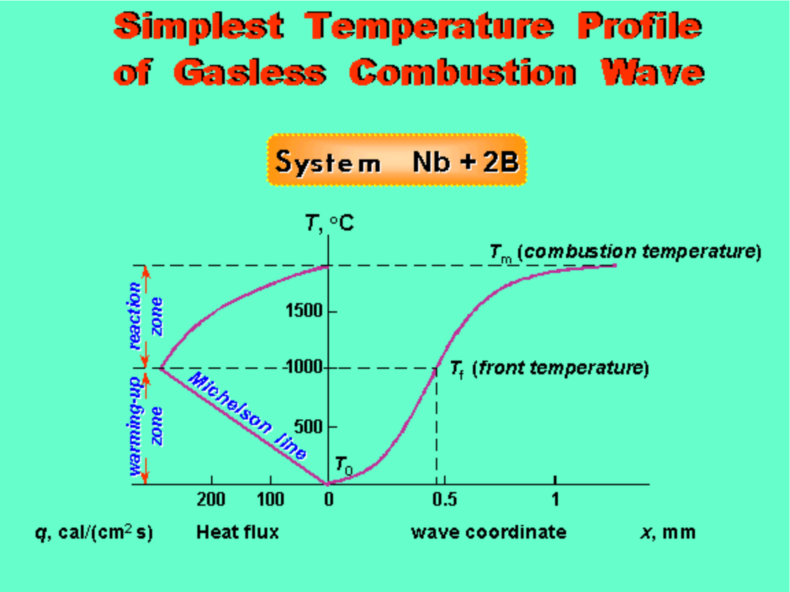


Fig. 6

### 3 .5.Front wave and post-processes

In the combustion wave occur various chemical, physical and physico-chemical processes in their totality provide the necessary heat. The wave has a certain length and consists of a series of zones:

- heating zone or preflame zone (combustion reaction it still did not leak, but only provided heat transfer and heating charge)
- reaction zone (in which the main flow of the combustion reaction, providing the necessary heat dissipation)
- afterburning zone (in which chemical reactions going on, but they do not affect the speed of propagation of the front)
- zones (stages) of the secondary physical and chemical transformations that define the structure and composition of the final products.

Spread zone of chemical reactions called the combustion wave. Front - a conditional surface separating the heating zone and the reaction (the cutting edge of high-temperature zone of the wave). Passage of the combustion wave is the main stage of SHS. Popular formula:

**SHS = + burning structure formation,**

secondary physicochemical transformations constitute the second stage of SHS.

### 3 .6.Key characteristics

The process of wave propagation is characterized by:

- extinction limit (between the parameters of the system, separating the two situations: the wave propagation and the lack of combustion under all conditions of initiation)
- buckling limit (between the parameters of the system, sharing regimes and unstable stationary combustion)

- propagation velocity of the front,
- the maximum temperature and
- heating rate in the wave stationary combustion,
- in unstable processes - frequency ripple speed hearth helical path, the value of the superadiabatic effect, etc.
- depth chemical transformation of initial reagents in the final products (combustion completeness)
- nonequilibrium combustion product characterizing incomplete phase and structural transformations in the process, the cooling rate of the combustion products (rare).

Most often realizable values of certain characteristics of SHS process:

| **The burning rate** | **0.1-20 cm / s** |
|---|---|
| **Combustion temperature** | 2300-3800 K |
| **Heating rate in the wave** | $10^{3}$ -$10^{6}$ deg / s |
| **Power Plug** | 10-200 cal / (cm $^{2)}$ |
| **Ignition delay** | 0.2-1.2 with |
| **Ignition temperature** | 800-1200 K |

Due to the high values of the velocity and temperature of combustion and heating rate in the wave of SHS is classified as extreme chemical processes.

### 3 .7.Chemical classes of reactions SHS

SHS processes for the chemical nature of the reagents directly irrelevant - only important value of the heat effect of the reaction and the laws of heat and heat transfer, the aggregate state of the reactants and products, the kinetics of phase and structural transformations and other macroscopic characteristics of the process. Therefore chemistry SHS processes varied. The most widely used

- the synthesis reaction of the elements

$Ti + C = TiC$

$Ni + Al = NiAl$

$3Si + 2N_2 = Si_3N_4$

$Zr + H_2 = ZrH_2$

- redox reactions

$B_2O_3 + 3Mg + N_2 = 2BN + 3MgO$

$B_2O_3 + TiO_2 + 5Mg = TiB_2 + 5MgO$

$MoO_3 + B_2O_3 + 4Al = MoB_2 + 2Al_2O_3$

$3TiO_2 + C + 4Al = TiC + 2Al_2O_3$

$2TiCl_4 + 8Na + N_2 = 2TiN + 8NaCl$

- oxidation of metals in complex oxide environments

$3Cu + 2BaO_2 + 1/2Y_2O_3 + 0.5 (1.5 - x) O_2 = YBa_2Cu_3O_{7-x}$

$Nb + Li_2O_2 + 1/2Ni_2O_5 = 2LiNbO_3$

$8Fe + SrO + 2Fe_2O_3 + 6O_2 = SrFe_{12}O_{19}$

Also known SHS reaction

- Synthesis of compounds

$PbO + WO_3 = PbWO_4$

- interaction decomposing compounds with elements

$2TiH_2 + N_2 = 2TiN + 2H_2$

$4Al + NaN_3 + NH_4Cl = 4AlN + NaCl + 2H_2$

- thermal decomposition of the complex compounds

$2BH_3N_2H_4 = 2BN + N_2 + 7H_2$

## 4. Products

And characterized by a variety of micro-and macrostructures.

### 4 .1. Morphology and macrostructure

SHS Products solids represent an arbitrary shape in different sizes. This different dispersion of the powders weakly associated aggregates of particles, foams , specs and ingots with different strength, films, fibers , crystals. Mass of products depends on the initial values and, to some extent, from the mechanism of the process.

In mixed systems macrostructure usually homogeneous in hybrid (gas-porous body) in the presence of filtration difficulties may occur composition distribution over the cross section of the sample after SHS.

In special cases, deliberately creating heterogeneous macrostructure combustion product (obtaining multilayer and functionally graded materials ).

### 4 .2. Composition

Chemical and phase composition of the products is determined by the composition of the source systems, their state diagrams, combustion efficiency, cooling conditions (cooling).

Impurity composition of the products is determined not only the purity of the reactants, but depends on the depth of the combustion process with self-cleaning. Products obtained under optimal conditions, characterized by high purity of unreacted starting material and the impurity oxygen.

### 4 .3. Microstructure

SHS products are usually polycrystalline structure with a crystallite size of 1-5 microns. Known examples of the preparation of nanosized (and amorphous), as well as coarse structures (with crystal sizes of up to 3 mm).

Crystallite sizes depend on the rate of cooling of the sample after combustion and kinetics of crystallization and recrystallization processes.

The porosity of the solid (non-dispersible) combustion products can vary from nearly zero (compact material) to high (90-95%, foams).

## 5.Management techniques

Objectives:

- Control the speed, temperature and completeness SHS process
- Composition of the structure and accordingly the properties of SHS-products.

Purpose:

- Optimization of SHS to meet the requirements in certain cases.

Management techniques:

- Impact on the characteristics of SHS (see paragraphs. 2 and 3) of the basic parameters of the initial charge (batch composition, the particle size of the reactants, the density, the size and initial temperature of the charge, the nature and concentration regulating additives and excipients), as well as the combustion conditions (composition and ambient pressure, the effect of electrical, electromagnetic and gravitational fields, mechanical stress) using the preliminary studies and the known general laws.

## 5. Conduct work

Initially were trained powder s, which were selected L A2O3 and TiO 2, and then they were mixed in various proportions with B and sent to the mill (results in table 1)

Table 1. Dependence of particle size (nm) of the speed (Hz)

| | La2o3 | TiO2 |
|---|---|---|
| 0 | 33.6 | 79 |
| 10 | 22.8 | 71.7 |
| 20 | 17.5 | 72.7 |
| 30 | 20.4 | 66.4 |
| 40 | 20 | 64.3 |

According to the results that blitz a schedule (Fig. 1), n is not that the particle size is not linearly dependent on the speed of the mill, as well was monitored initiation temperature dependence of the speed given in Table 2 and a schedule (Fig. 2)

Table 2. initiation temperature dependence on the rotational speed

| | 5 minutes | | 10 minutes | | 15 minutes | | 20 minutes | | 25 minutes | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Institute | max | Institute | max | Institute | max | Institute | max | Institute | max |
| 0 | 540 | 707 | 558 | 708 | 548 | 712 | 551 | 685 | 557 | 779 |
| 10 | 540 | 732 | 561 | 738 | 550 | 766 | 533 | 723 | 529 | 777 |
| 20 | 478 | 712 | 456 | 787 | 462 | 723 | 463 | 720 | 495 | 749 |
| 30 | 490 | 729 | 480 | 751 | 475 | 720 | 467 | 771 | 552 | 782 |
| 40 | 517 | 765 | 526 | 714 | 508 | 727 | 576 | 785 | 555 | 802 |

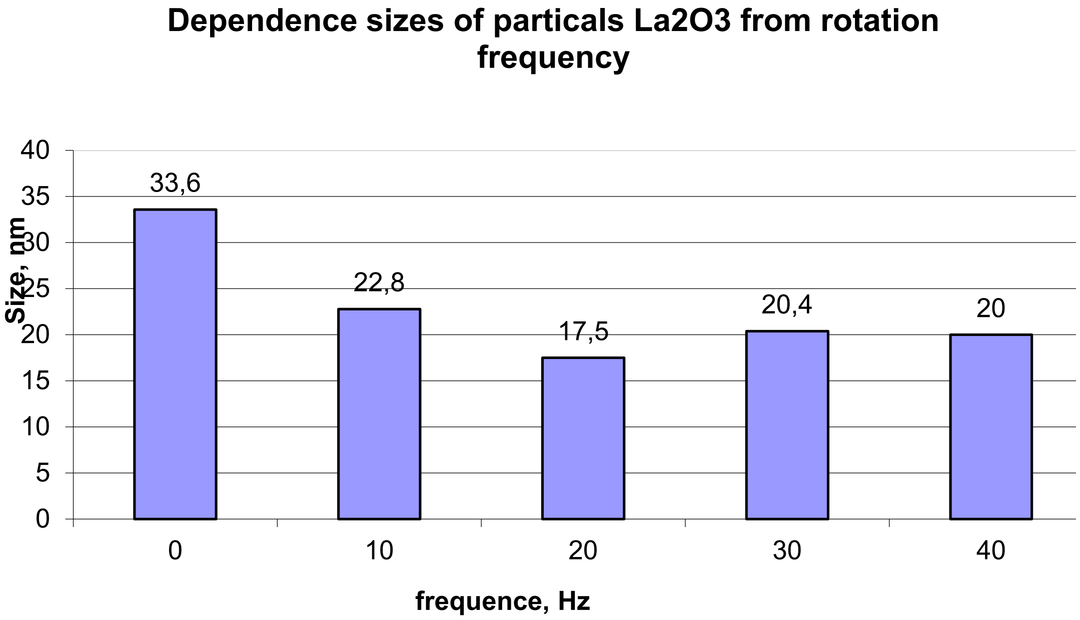


Fig.1 Dependence of particle size on the speed

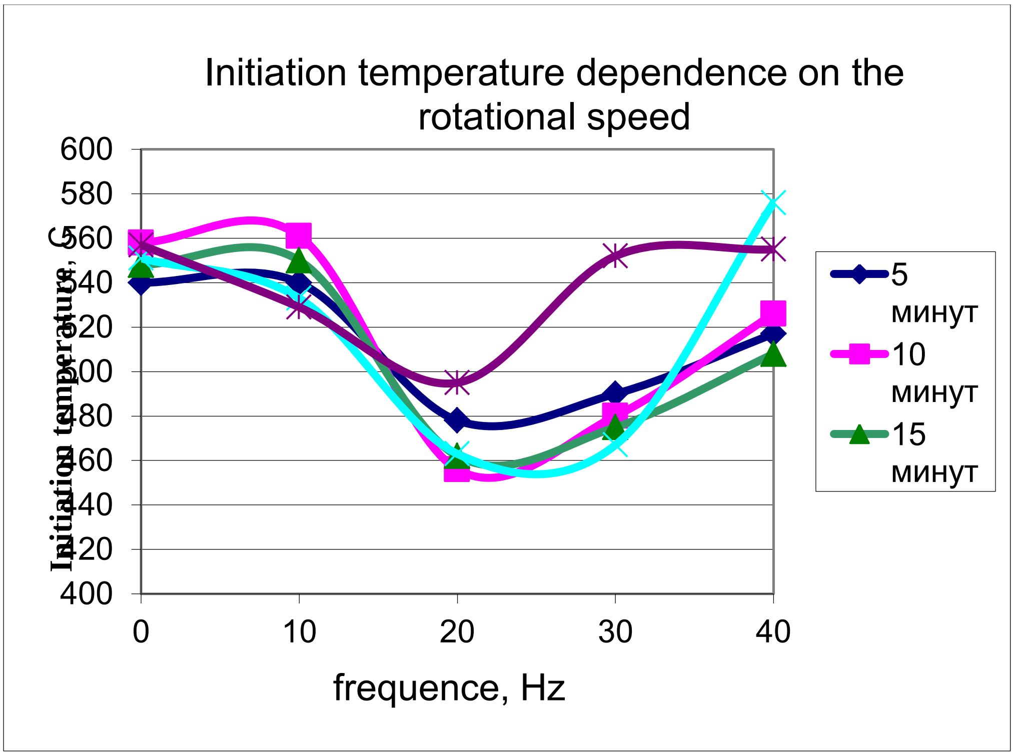


Fig. 2 . initiation temperature dependence on the rotational speed

From the graph, we can see that the minimum temperature attained in rotational frequency of 20 hertz, it may be explained by the data of Table 1, namely that for a given speed is reached the minimum size of particles, which in turn:

- leads to disruption of the integrity of the materials and increase the free surface of the substances;

- causing elastic deformation of the plastic. The relaxation of residual stresses and deformations in solids at low temperature occurs slowly enough, and therefore, the substance by the action of mechanical forces dvergnutoe some time margin has "excess" energy;
- distortion of the crystal lattice of the mineral that is the cause of point d efekt and linear dislocations;
- violation of the integrity of the crushed material leads to the rupture of chemical bonds of matter;

T ak during a research work was conducted burning mixtures obtained (in the form of compressed tablets) prepared by SHS and refine the composition shown in Table 3.

Table 3. Results combustion substances

| Composition | without NiAl | time, min | serial numbers | La2O3 | LaBO3 | LaB6 | TiO2 | TiB2 | B2O3 | B | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10Hz | | 5 | 1 | 16.7 | 18.6 | 1.3 | 30 | 0.5 | 2 | 30.9 | 100 |
| | | 10 | 2 | 14.2 | 35.5 | 0.7 | 19.6 | 2 | 3 | 25 | 100 |
| | | 15 | 3 | 3 | 64.9 | 3 | 5.1 | 10 | 4 | 10 | 100 |
| | | 20 | 4 | 5 | 57.6 | 2.4 | 15 | 12 | 2 | 6 | 100 |
| | | 25 | 5 | 8 | 63 | 1.1 | 10.3 | 7 | 2 | 7 | 98.4 |
| 10Hz | | | | | | | | | | | |
| | c NiAl | | | La2O3 | LaBO3 | LaB6 | TiO2 | TiB2 | B2O3 | B | |
| | | 5 | 1 | | 15.1 | 3.3 | 15.8 | 6.3 | 6.5 | 53 | 100 |
| | | 10 | 2 | | 14.2 | 63.1 | 3.2 | 11.5 | | 8 | 100 |
| | | 15 | 3 | 5.6 | 1.7 | 65 | 3.7 | 15.7 | 6.3 | 2 | 100 |
| | | 20 | 4 | 7.1 | 2.7 | 58 | 3.4 | 13.3 | 12.5 | 3 | 100 |
| | | 25 | 5 | | 31.7 | 43 | 3.3 | 13 | | 9 | 100 |

After the first series of combustion was found that the residue of unburnt boron is relatively high, it was decided to add NiAl. Reaction did not pass without the addition of nickel delayed at an intermediate stage (Education LaBO 3)

The table also shows that after addition of NiAl In the residue decreased significantly and in the 15th minute we get optimum reduction of unnecessary impurities up to 2 percent due to activation and Ni.

Conclusions: During the work done were identified ways to control SHS processes by changing the SAF system, were also discussed in more detail the parameters themselves, and implemented a series of test batches of different compositions and variations of the basic mixture that after it was implemented in the tables and graphs

Recommendation: Continue to study and experiment to find the optimal share e NiAl added to optimize the SHS process to obtain thehighest possible purity of unreacted starting in eschestvam and oxygen impurity in the self-cleaning process.

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