

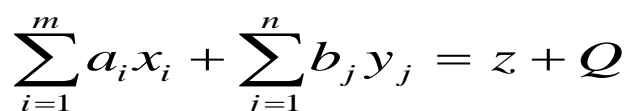
Lecture 11. Self-propagating high temperature synthesis (SHS). SHS thermodynamics

The purpose of the lecture: to familiarize students with the process of self-propagating high-temperature synthesis, its parameters and thermodynamics.

Expected results: students gaining knowledge about the process of self-propagating high-temperature synthesis, its parameters and thermodynamics.

In recent years, the SHS process of refractory compounds has become widespread in chemical technology. The essence of the process is conveniently explained in the following simple example. A cylindrical sample is compressed from a mixture of metal powders, such as titanium, and non-metal, such as soot. A thermal pulse is applied to the sample from one end. A chemical reaction is excited in the surface layer of the sample and a synthesis wave is formed, which then propagates along the axis of the sample at a constant speed. Wave propagation is accompanied by a bright glow. As a result, in a very short time (seconds), the initial mixture of powders turns into a synthesized compound (in this case, titanium carbide).

The generalized chemical scheme of the most common SHS process has the form



x = Ti, Zr, Hf, V, Nb, Ta, Mo, W, etc.

y = B, C, N₂, Si, S, Se, Al, etc.

z = borides, carbides, nitrides, silicides, chalcogenides, solid solutions, etc.

Elements X are metal powders, and Y are non-metals that are used in powder, liquid or gaseous state. Z products are a refractory compound and are usually found at solid state combustion temperatures. Chemical interaction of elements proceeds in the condensed phase even if one of the reactants is gas.

In most combinations, the interaction of X and Y occurs with the release of a large amount of heat and is strongly activated, which determines the possibility of combustion - the numbers β and γ are quite small.

Currently, three types of SHS have been studied. These are mixed condensed systems (powder mixtures), cryogenic condensed systems (liquefied gas is used as reagent Y) and hybrid systems - a powdered metal - gaseous non-metal. Some parameters of SHS processes are given in table 11.1.

It can also be emphasized that sometimes high pressures (thousand atmospheres) are created or achieved. All this suggests that SHS should be classified as the so-called extreme processes.

Table 11.1.

Physical parameters of SHS processes

The maximum temperature in the synthesis wave	$T_M=1500-4000\text{ }^\circ\text{C}$
Synthesis wave propagation speed	$\eta=0,5-15\text{ cm/s}$
Synthesis Zone Thickness	$L=10^{-2}-5\cdot 10^{-1}\text{ cm}$
The heating rate of a substance in a wave	$W=10^3-10^6\text{ deg/s}$
Initiation power	$q_0=10-100\text{ cal/cm}^2\text{ s}$
Initiation duration	$T=0,05-5\text{ s}$

It should be noted that in recent years the following areas of SHS have been actively developing

- SHS-powder technology (in the production of abrasive and ceramic materials, metal alloys, hard alloys, when applying various protective coatings, etc.)

- SHS technology of refractory materials and complex oxides (refractories and coatings from them to protect parts of metallurgical equipment and oxides for growing single crystals for the needs of electronic equipment)
- SHS metallurgy (casting and smelting)
- Production and use of ferroalloys nitrided by SHS method
- SHS welding (for receiving one-piece products)
- Gas transport SHS coatings (for coatings from nitrides, borides, metal silicides, intermetallic compounds)
- SHS catalysts and catalyst supports
- SHS pigments.

The natural further development of SHS is associated with obtaining valuable substances and materials directly from mineral resources, as well as the use of metallurgical and mining industry waste as raw materials for SHS technology.

This requires a new set of studies in the field of:

- physico-chemical analysis - diagnostics and identification of raw materials and industrial waste
 - structural macrodiagnostics of processes occurring during the propagation of heat waves and heterogeneous condensed matter
 - chemical physics, thermophysics, physical mechanics of SHS products
 - modeling of structural macrokinetics.

Almost all combustion features are associated with a strong exothermic process. It causes high reaction temperatures that occur solely as a result of self-heating. For the implementation of combustion, it is necessary to spend a negligible amount of energy on the initiation of processes - the process itself is completely due to the internal energy capabilities of the system. The lack of energy costs is an important technological indicator of the combustion process. The simplicity and reliability of the equipment associated with the fact that there is no need to enter energy from the outside.

The main objective of the SHS process is to obtain materials and products with desired properties. This determines the importance of research to clarify their mechanism and the more interest they deserve. From the point of view of chemical kinetics, the study of the mechanism means the identification of the stages of the process, as well as intermediate products.

The study of the SHS mechanism is carried out in three directions.

1) the study of the laws and conditions of the propagation of the synthesis wave, the determination of the physical parameters of the process, the study of the stability of stationary modes of wave propagation and the conditions for the occurrence of an unsteady (self-oscillating) wave pattern, the determination of heat transfer, the level of heat loss, filtration rate, etc.

2) physical and chemical studies that establish the relationship: the speed and completeness of SHS implementation, the study of the mechanism of phase formation and structure formation (the development of transformations not only in time but also in space)

3) study of the mechanism of a chemical reaction in a synthesis wave.

Such studies are extremely difficult. Firstly, due to the transience of all phenomena, as well as the high temperatures at which they occur. Secondly, due to the limited methodological capabilities.

There are stationary and non-stationary combustion modes; self-oscillating spin, the dispersion rate, reagent ratio, initial T_0 , etc.

The chemical mechanism of the transformation of substances is complex, the process of formation of the final products consists of a series of sequential and parallel stages, while stable intermediate products can be isolated by quenching.

SHS thermodynamics

Combustion in an isolated adiabatic system is characterized by the fact that the enthalpy of the initial mixture at the initial temperature T_0 is equal to the enthalpy of the final products at the combustion temperature T_{ad} . This circumstance makes it possible to thermodynamically calculate the composition of the products and the combustion temperature.

$$\sum_{i=1}^n [H(T_{ad}) - H(T_0)]_i = Q$$

If a single product is formed in the SHS process, the calculation is reduced to determining only the combustion temperature. The expression for calculating T_{ad} has the form

$$\int_{T_0}^{T_{ad}} C(T) dT = Q - \sum_{i=1}^n \mu_{\Phi} H_{\Phi} \quad (1)$$

$\mu_i = 0$ for $T_{ad} < T_F$; $\mu_{\Phi} = 1$ at $T_{ad} > T_F$

C is the heat capacity of the product,

Q is the heat of formation of the product (at T_0);

T_F and N_F - respectively, the temperature and heat of the phase transition in the product,

μ_{Φ} is the fraction of the higher temperature phase in the product at $T_{ad} = T_f$; n is the number of phase transitions.

The values of $C(T)$ and Q are found from the reference data. Using expressions for the average heat capacity and thermal effect of the process

$$\bar{C} = \frac{1}{T_{ad} - T_0} \int_{T_0}^{T_{ad}} C(T) dT; \quad Q_{np} = Q - \sum_{i=1}^n \mu_{\Phi} H_{\Phi} \quad (2)$$

in (2) instead $\int_{T_0}^{T_{ad}} C(T) dT$ we substitute Q_{np}

$$T_{ad} = T_0 + Q_{np}/C \quad (3)$$

$$\text{At } T_{ad} = T_{\Phi} \quad \mu_{\Phi} = [Q - \bar{C}(T_{\Phi} - T_0)] / H_{\Phi} \quad (4)$$

These simple expressions explain many experimental facts related to the influence on T_g of the initial temperature, forming, ratios of reagents, dilution of the mixture with the product, in particular, the presence of steps on the $T_g(T_0)$ curves.

This approach has found wide application for estimating the temperature of SHS processes from elements. The general approach considers chemical and phase equilibria in multicomponent combustion products, which makes it possible to consider not only the temperature, but also the composition of the products.

Based on the calculations, a large number of high-temperature SHS processes were revealed in which $T_{ad} > 3000$ K. The calculated values often exceed the experimental ones by 200-400 K, due to the fact that adiabatic temperatures were not provided in the experiments. $T_{ad} < T_m$ for example $Ti + Al$, $Fe + Ti$, then SHS at $T_0 = 298$ K is unlikely, for the implementation of SHS it is necessary to increase the initial temperature. $T_{ad} = T_m$; $Ni + Al$; $Co + Al$ - under normal conditions $T_{ad} > T_m$.

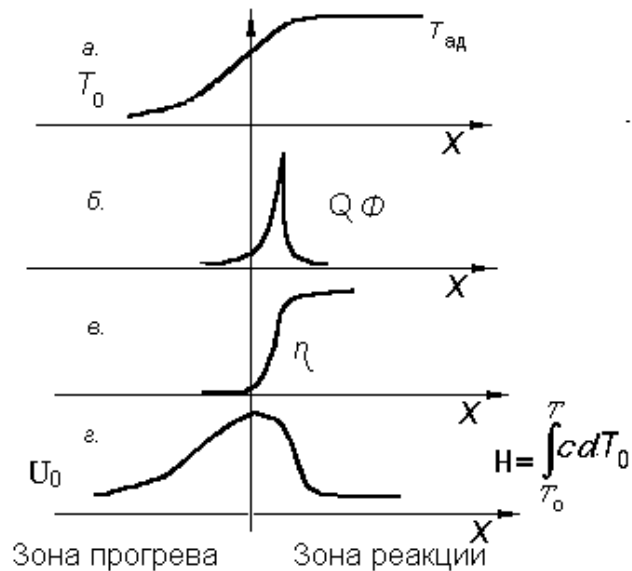
The stationary adiabatic propagation of a plane wave can be described using a system of equations

$$\lambda \frac{d^2 T}{dX^2} - C_p U \frac{dT}{dX} + Q_p \Phi(T, \eta) = 0 \quad (5)$$

$$-U \frac{d\eta}{dx} + \Phi(T, \eta) = 0 \quad (6)$$

with conditions $x = -\infty \quad T = T_0 \quad \eta = 0 \quad x = +\infty \quad T = T_{ад} \quad \eta = \eta_p$.

From the solution of equation (5), (6), a typical wave structure follows.



The heat release rate reaches a maximum at temperatures close to $T_{ад}$; the reaction is much smaller (Q_f) of the heated layer, the temperature profile is wider than the concentration profile, the total enthalpy in the wave is higher than in the starting materials and reaches a maximum at the end of heating.

Literature

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