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Combustion in a System of Conjugated Layers and High-Temperature Synthesis of Materials

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Abstract—The possibility of constructing layered systems for high-temperature synthesis of materials is demonstrated. The cases of vertical and horizontal arrangement of layers, which ensure different types of a technological combustion of the initial reactant mixtures with or without subsequent interaction of the reaction products formed, are considered. The conditions are found for the synthesis of alkaline-earth metal titanates and aluminum borides in the layered systems.

The temperature of the combustion wave front in metal–oxide systems may be as high as (3–4) × 10^3 K under quasi-adiabatic conditions. In order to perform a high-temperature synthesis, conditions of this kind can be created if the mixture of reacting components is formed as a layer receiving thermal energy from the side of parallel energy-carrying layers [1].

A stack of layers selected with account of the task to be accomplished is arranged horizontally or vertically (perpendicularly to the horizontal or vertical axis, respectively). In some cases, it can be subjected to the action of a centrifugal force, or an electric or a magnetic field.

This article is concerned with the fundamental aspects of combustion of complex stacks in relation to the mutual arrangement of the constituent layers, their orientation, etc. It is not aimed to establish a strict relationship between the kinetic parameters that govern the chemical process and the parameters determining the removal of heat from the reaction zone. The goal is to consider the phenomenology of combustion in the layers and the propagation of the combustion front in the adjacent layers.

Combustion of a horizontal stack of layers. In the horizontal variant, when the layers are arranged perpendicularly to the horizontal axis (Fig. 1a), the products formed in combustion of oxide system and, in particular, reduced metals, do not penetrate into the adjacent layers. In this case, only conductive heat transfer occurs, since the horizontal stack is composed of chemically independent layers. To ensure a quasi-adiabatic course of the process in the layered system, ignition is performed simultaneously in the adjacent layers. Then the synthesis layers can be repeatedly alternated with the layers that serve as sources of heat, with the maximum heating achieved.

The macrokinetics of combustion in a layer is determined not only by the reactant concentrations, temperature, and pressure, but also by external forces, e.g., those due to centrifugal acceleration in the case of axial rotation.

The characteristic time τ of combustion of a stack is constituted by the times τ_k of burning-through of all

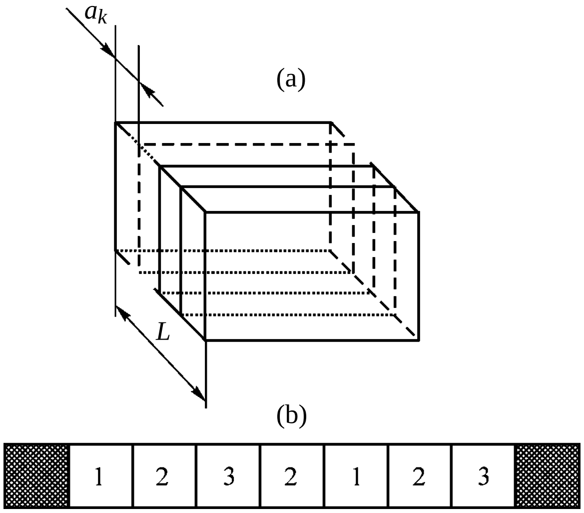

Fig. 1. Schematic of a horizontal stack of layers. Stack: (a) that in the general case and (b) that with a repetitive system of three layers, in which layer no. 2 is the synthesis layer.

the k layers of the stack:

$$\tau = \sum_{k=1}^{i} \tau_k = \sum_{k=1}^{i} (n\overline{M}/W_k), \qquad (1)$$

where n is the number of moles; $\overline{M}$, average molecular weight of the starting substances; and W_k, mass rate of the overall reaction in the kth layer.

The normal combustion velocity U_k in a layer is equal to the thickness of each layer (a_k) divided by the time τ_k of its combustion, and, consequently, the average linear velocity of combustion of the whole stack ($\bar{U}$) in the case of successive ignition of the layers is given by

$$\bar{U} = \tau^{-1} \sum_{k=1}^{i} a_k. \qquad (2)$$

Let us assume that the optimal result of synthesis is determined by the average mass velocity of combustion of a stack with substance density ρ_k in the kth layer:

$$\bar{U}_{\mathrm{m}} = S\tau^{-1} \sum_{k=1}^{i} a_k \rho_k. \qquad (3)$$

The quantity $\bar{U}_{\mathrm{m}}$ differs from the additive $\bar{U}_{\mathrm{am}}$, which is equal to the average velocity of separate combustion of each layer of the stack at average temperature T_{av},

$$\bar{U}_{\mathrm{am}} = S \sum_{k=1}^{i} (a_k \rho_k / \tau_k).$$

Let us name the ratio

$$\varphi = \bar{U}_{\mathrm{m}} / \bar{U}_{\mathrm{am}} \qquad (4)$$

the coefficient of conjugation of layers in a stack. This coefficient characterizes the rise in the rate of the overall reaction in a stack, caused by changes in the heat transfer conditions, number and distribution of ignition points, and mutual arrangement of layers in the stack:

$$\varphi = f(\lambda, \rho, S, P_n), \qquad (5)$$

where λ is the heat conductivity; S, cross-sectional area of the stack; P_n, nth permutation, whose total number P_n in a stack composed of k layers is given, with account of the fact that the 1st, 2nd, 3rd, ..., and kth layers are repeated α, β, γ, ... times, by

$$P_n = k!/\alpha!\ \beta!\ \gamma!,... \qquad (6)$$

It is noteworthy that the quantity φ we introduced also characterizes the synthesis layers. In this case, the quantity $\bar{U}_{\mathrm{am}}$ is equivalent to the rate of accumulation of the product at T_{av}, and $\bar{U}_{\mathrm{m}}$, to the rate of its accumulation in a layer within a stack.

Thus, for any composition of the stack, the value of φ depends on the arguments in expression (5), whose variation mainly affects $\bar{U}_{\mathrm{m}}$. If the parameters λ, ρ, and S are constant within the limits of variations, then the only reason why the coefficient φ changes is transition from one arrangement of the layers to another. The best synthesis effect, to which corresponds the maximum value of φ, is achieved at a certain average value of the mass velocity.

Let us consider a three-layer system repeated in the stack k times (see Fig. 1b). Layer 2, in which the strongest heating conditions are to be created, is in contact with layer 1 on the left and layer 3 on the right. In the case of a simple, nonchain reaction in layer 2, the degree of conversion of the reaction mixture at any point of this layer along the stack axis is determined by the temperature distribution on the left and on the right, attained by the instant of time τ_k. The value of φ in layer 2 is determined in this case by the velocity U_{m} of the heat wave that arrives from the adjacent layers.

The resulting value of φ for the three layers combined is given by

$$\varphi = \overrightarrow{\varphi}_1 - \varphi_2 + \overleftarrow{\varphi}_3.$$

The strongest effect ($\varphi' = 0$, $\varphi'_2 = 0$) corresponds to a numerical equality of the velocities of the oppositely propagating combustion waves in layers 1 and 3:

$$|U_{\mathrm{m}_1}| = |U_{\mathrm{m}_3}|.$$

The temperature distribution within layer 2 is set by the propagation of the heat waves from the left and from the right. If it is assumed that the total content of enthalpy in layers 1 and 3 much exceeds the heat consumed by the reaction in layer 2, then the reaction rate profile in the synthesis layer is determined by the existing temperature distribution. If, further, the characteristic time of the reaction in the synthesis layer is of the same order of magnitude as the time of propagation of the heat wave (the reaction begins at its front), then the temperature profile is approximately described by the known Michelson distribution:

$$T_{(x)} \approx T_0 + (T_c - T_0)\exp UXC_t\rho/\lambda. \quad (7)$$

At the point x where the temperature increases by a factor of approximately e ($T_x/T_0 \approx 2.718$ at $T_0 \approx$ 300 K), but the reaction rate can still be neglected,

$$(T_x - T_0)/(T_c - T_0) \approx e, \quad (8)$$

$$x \approx \lambda/(UC_p\rho).$$

For the TiO_2–Al reaction mixture diluted with graphite, C_p = 170 J g^{-1} deg^{-1}, λ = 0.05 J cm^{-1} deg^{-1} s^{-1}, ρ = 2.3 g cm^{-3}, U = 0.02 cm s^{-1}, and the increase in temperature to $T_x/T_0 \approx 2.718$ will occur at a distance $x = 1.5 \times 10^{-3}$ cm from the plane that divides the reaction and heating layers.

In various mixtures of metal oxides with the specific heat $C_p \approx$ 80–130 J g^{-1} deg^{-1}, all other conditions being the same, the value $x \approx (1–2) \times 10^{-2}$ is reached within 1 s, and at U = 1 cm s^{-1}, at 10^{-3} s. Extrapolation suggests that a layer of thickness 10 cm is heated in 1 s. Since the synthesis layer can be heated both from the left and from the right, the yield of the reaction product is the highest at the boundary of the heat source and the lowest in the middle of the synthesis layer.

The ratio (4) of the mass velocities characterizes rather effectively the relationship between the thermal properties of layers for a three-layer stack, in which the yield of the product is determined by temperature.

Let us assume that at a furnace temperature T_1 the reaction rate in the synthesis layer is infinitely small and the velocity of the combustion wave in the auxiliary layer is U_1. The combination of two auxiliary layers and the synthesis layer that lies in between is a system in which several pathways of the process are possible, depending on the heat-exchange conditions. If the synthesis layer considerably exceeds in mass the auxiliary layers and the contact area is small, then the middle layer acts as a heat insulator, the relative yield of the reaction product in this layer is nearly zero, and φ tends to unity. As the mass of the synthesis layer decreases and the contact area increases, the conditions can be created under which the reactions in the layers of the system go to completion and the velocity of the combustion wave in isolated auxiliary layers is zero. This is the ideal, hardly achievable in practice, case, when φ tends to infinity.

Real layered systems include auxiliary layers in which, when these layers are in the isolated state, the combustion process occurs in the steady-state mode without any change in their shape or disruption of the integrity of their surface, the loss of heat across the lateral surface is at a minimum, and the amount of thermal energy released is sufficient for initiating or maintaining reactions in the synthesis layer.

Synthesis of titanates of alkaline-earth elements in a horizontal stack. The reaction of titanium and barium oxides occurs in the temperature range 1350–1450°C. The composition and parameters of the auxiliary layer were chosen taking into account the endothermic effect of the reaction between the components in the main layer and its geometric dimensions [2].

The starting mixtures were thoroughly mixed. A hydraulic press equipped with a pressure gage for recording the compaction force was used to fabricate samples in the form of cylinders of various diameters or prisms, depending on the aim of a particular experiment. The samples were used to form layered systems, which were then placed in a furnace heated to the temperature of self-ignition of the mixtures used. After the combustion in the auxiliary layers was complete, a sample was either extracted for cooling in air or left in the furnace until equalization of temperatures.

In the case of synthesis of materials of prescribed composition for electronics, the requirements imposed on the product purity are high, and not only chemical interaction between the layers, but even mechanical penetration of the combustion products formed in the auxiliary layer into the synthesis layer are unacceptable. Therefore, the layers were arranged vertically, along the common horizontal axis. The cylindrical shape of the multilayer compound structure was chosen in order to diminish the area of contact with the substrate and, accordingly, to make lower the unproductive heat expenditure. These conditions ensure a sufficiently high ratio of the total weight of the reactants to the total area of the sample surface, across which heat is consumed, and the maximum possible area of contact between the layers. As a result, a steady-state combustion wave was obtained in the auxiliary layer and the most complete energy transfer from one layer to another was achieved. The furnace temperature was maintained at 850°C.

In the course of the experiments, auxiliary layer compositions Al–Cr_2O_3 with varied content of the reducing agent were studied. At a constant layer diameter of 20 mm and an auxiliary to synthesis layer mass ratio of 2, it was found that the temperature to which the reagent mixture in the synthesis layer is heated varies with the composition and mass of the auxiliary layer. The results obtained are listed in Tables 1 and 2.

The limiting mass ratio in a synthesis layer of composition TiO_2–$BaCO_3$ and an auxiliary layer of composition Al–Cr_2O_3 was 1 : 2 at an aluminum content in the initial composition of the auxiliary layer of 15% and 1 : 1 at 23%. An X-ray phase analysis demonstrated that the finished product in the synthesis layer is the tetragonal modification of barium titanate.

In a similar way, with a minimum energy expenditure, we synthesized magnesium and calcium titanates. In this case, experimental selection of the composition and weight of the layers ensured that, in accordance with a calculation, the temperature in the synthesis layer was as high as 1650–1700°C at the furnace temperature of 850–900°C.

Synthesis of pure strontium titanate is hindered by the inertia of the process. To bring its rate in correspondence with the reaction rates in the auxiliary layers, the stock of the main layer was mechanically activated (the efficiency of this process was demonstrated in preliminary experiments for the example of an Al–Cr_2O_3 mixture [3]).

Thus, the approach developed for synthesis of materials in a layered system was used to obtain a number of compounds whose conventional synthesis involves complicated preparation of starting reactants and prolonged thermal treatment at high temperature. Combining the layer technique with such methods as, e.g., compaction or mechanochemical activation of the starting mixtures makes it possible to improve the control over the process.

Synthesis of aluminum borides in a stack of layers with protective interlayers. In contrast to the case of synthesis of alkaline-earth metal titanates, when it is only important to observe the lower temperature limit, synthesis of aluminum borides of certain compositions, AlB_2, AlB_{10}, and AlB_{12}, is complicated by its rather narrow temperature range (°C):

AlB_2	1000–1100
α-AlB_{12}	1100–1550
β-AlB_{12}	1550–1660
AlB_{10}	1660–1850

Moreover, aluminum borides are, as a rule, formed in the presence of carbon, which takes the uncompensated free bonds of complex boride molecules, and contamination of the finished product with other impurities, which diffuse from the auxiliary layers, significantly changes the electrotechnical properties of the borides.

Table 1. Heating temperature T_{comb} of the synthesis layer in relation to the stock composition of the auxiliary layer

C_{Al}, wt %	Forming density ρ, g cm^{-3}	T_{comb}, °C
12.0	2.726	1250
15.0	2.828	1382
18.0	2.830	1510
20.0	2.726	1648
23.0	2.725	1650
26.5	2.718	1618
32.0	2.692	1600

Table 2. Heating temperature T_{comb} of the substance in the synthesis layer in relation to the weight *m* of the auxiliary layer at aluminum content in this layer of 18%

m, g	Cylinder height *h*, mm	T_{comb}, °C
1.84	2.55	1406
3.80	4.46	1470
5.74	6.84	1538
7.64	8.98	1550
9.81	11.0	1580

The low-temperature boride AlB_2 was synthesized in a furnace heated to 870°C in an Al–B_2O_3 layer with additional heating from the side of an auxiliary layer composed of a stoichiometric mixture (Al + V_2O_5): Al_2O_3 (20–25%)–(Al + V_2O_5) (80–75%) or V_2O_5 (20–25%)–(Al + V_2O_5) (80–75%). AlB_{12} was synthesized using a three-layer system with two auxiliary layers situated on both sides of the main layer in which the Al–B_2O_3 mixture is also used as the synthesis layer, and the Al–TiO_2 system with nearly stoichiometric composition, as the auxiliary layer. The furnace temperature was 950°C, and the temperature in the combustion wave, 1500–1600°C.

Further rise in temperature enhances the diffusion interaction between the layers. Titanium penetrates from the auxiliary layer into the main layer and reacts with boron to give titanium boride. To preclude this process in synthesizing AlB_{10}, insulating interlayers of activated carbon were used. The use of inert high-melting interlayers enables a choice of the spatial arrangement of the layered compound structure, a horizontal or a vertical stack. The temperature in the reaction zone was raised by increasing the number of alternating layers in the order 1–2–3–2–1–2–3– etc.

(see Fig. 1b). To improve the mechanical strength of the system, a horizontal arrangement of the layers along a common vertical axis was used. Placing this multilayer system in a cylindrical graphite reactor ensures that the combustion process is highly adiabatic.

CONCLUSIONS

(1) The combustion of layered compound structures with characteristic conjugation of chemical processes in the layers was analyzed.

(2) It was shown that the main and fundamental distinctive feature of the layered combustion is the possibility of performing reactions in deep layers in a quasi-adiabatic mode. The temperatures that can be reached are as high as $(3–4) \times 10^3$ K.

(3) It was demonstrated that, in a horizontal stack with layers arranged perpendicularly to a horizontal axis, the combustion products of oxide system do not penetrate into adjacent layers, the layers are chemically independent, with only conductive heat exchange existing between them. As a characteristic of the compound structure was introduced the coefficient of layer conjugation, which is determined by the relative positions of the layers, changes in the combustion conditions in the case of combustion in a stack, and the number and distribution of ignition points; it characterizes the rise in the rate of the overall reaction. At a furnace temperature of 850°C, alkaline-earth metal titanates and aluminum borides were synthesized.

(4) With the layers lying one above another perpendicularly to a vertical axis, heavy reaction products in a melt pass from upper layers to lower ones and enter into a reaction with new reagents. This scheme is efficient in the case of a stage-by-stage formation of a multicomponent product and can also be used when insulating interlayers are introduced between the layers.

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