

**COMBUSTION OF POROUS MEDIUM AT SIMULATED GRAVITY:
EVOLUTION OF COMBUSTION FRONT STRUCTURE**

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A mathematical model of exothermic chemical transformation of high-caloric mixture under the terms of centrifugal forces is considered. The process is studied using the thermite composition of $3\text{NiO} + (2 + \alpha)\text{Al} \rightarrow \text{Al}_2\text{O}_3 + (3 - \alpha)\text{Ni} + \alpha\text{NiAl}$. Such processes are used in high-temperature synthesis to obtain target products in the combustion wave of the initial mixture. The process is characterized by combination of high-temperature combustion with liquid products formation, their separation and cooling in one technological approach. The difference of the model under study implies its pass-through description which allows analyzing interinfluence of separate stages on the process dynamics. It results in more adequate description of the process.

Key words: filtration combustion, thermite mixtures, centrifugal forces, separation, melting.

INTRODUCTION

The combustion process of high-caloric mixtures is used in the method of self-propagating high-temperature synthesis (SHS). The products of the process are melts. The products fluidity allows their further processing by external forces. The present investigation analyzes the combustion front structure and dynamics at the effect of external centrifugal forces.

During exothermic chemical transformation a multicomponent high-caloric mixture changes its chemical composition and rheology of reagent transportation to the reaction zone. Mathematical modeling and direct experimental study of the above mentioned mixture combustion is rather complicated due to the extreme terms of the process [1]. The model of gasless and filtration combustion allowed us to advance in our comprehension of the problem. But it isn't sufficient. The analysis of the models considering the "regulated" complexity of the composition, a great deal of phases (gas, liquid component with complicated rheology, solid porous frame (matrix)), separation of metal and ceramic components in the condensed medium is considered to be rather promising.

MATHEMATICAL MODEL

We'll use the property which is specific for nature, i.e. "let like be dissolved by like" – oxide by oxide, metal by metal. While developing the model of multicomponent chemically active continuous medium, we'll be able to separate three groups of the components: metal, ceramics, and oxidizing gas. Therefore (Fig. 2) we'll consider the three-rate, three-temperature model of combustion of a multicomponent mixture. In each group the space- and time-variable characteristics are determined by the laws of conservation of mass, momentum and energy. The process of exothermic chemical transformation is studied in accordance with ideology of Ya.B. Zeldovich and D.A. Frank-Kamenetsky [3].

The system of ($3\text{NiO} + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Ni}$, $\text{Ni} + \text{Al} \rightarrow \text{NiAl}$) will be used for our analysis. Macrokinetics of the interaction is rather complicated and to be studied separately. We'll deal with "truncate" description of the interaction kinetics which can be widened for some other interesting details. According to literature data solid NiO in β -phase is decomposed to metal nickel and oxygen at $T > 1503$ K:



By the time melted Al will appear in the porous composition in the warming-up zone of the synthesis front (Al melting point is 933 K, that of the surrounding oxide film Al_2O_3 is about 2300 K). The high-melting film is partially

dissolved and destroyed in the reactor but partially restored at centrifugal forces, at oxygen interaction with aluminum with heat release, Q:

Refractory film under the reactor's conditions partially dissolves and collapses, under the action of centrifugal forces, partially restored by the interaction of oxygen with aluminum and heat release Q:



Less fast and less exothermic stage forms intermetallic.



With the temperature increase the strong frame of the porous mass turns into the fluent liquid melt which moves to the initial porous medium. In the warming-up zone the penetration of the initial mixture is changed, and oxygen filtration to the low-temperature initial medium and liquid products is damped. The oxidizer concentration in the narrow reaction zone induces to apply a simplified kinetic scheme of gasless interaction instead of (1) and (2):



So behind the combustion front suspension of liquid metal, liquid ceramics and oxidizer is formed with some characteristic dimensions of the components (for simplicity we assume them to be equal to the initial data) and individual travel rate. Therefore, behind the combustion front a suspension of liquid metal, liquid ceramics and oxidizer is formed with some characteristic dimensions of the components (for simplicity we assume them to be equal to the original ones) and

individual rates of displacement. The reagents participating in the chemical transformation change their masses and therefore, the field of centrifugal forces. Taking into consideration that in the case of the condensed state the diffusive transfer is concentrated in the reaction zone and partially considered by macrokinetic description of chemical interaction velocity, we'll confine ourselves to convective mass transfer and mass exchange due to chemical interaction:

$$\frac{\partial \rho(\text{NiO})}{\partial t} = -2W_0(T)\mu(\text{NiO}) - \frac{\partial}{\partial x}(\rho(\text{NiO}) * v(\text{NiO})) \quad (5)$$

$$\frac{\partial \rho(\text{Al})}{\partial t} = -(4W_1(T) + W_2(T))\mu(\text{Al}) - \frac{\partial}{\partial x}(\rho(\text{Al}) * v(\text{Al})) \quad (6)$$

$$\frac{\partial \rho(\text{NiAl})}{\partial t} = W_2(T)\mu(\text{NiAl}) - \frac{\partial}{\partial x}(\rho(\text{NiAl}) * v(\text{NiAl})) \quad (7)$$

$$\frac{\partial \rho(\text{Ni})}{\partial t} = (2W_0(T) - W_2(T))\mu(\text{Ni}) - \frac{\partial}{\partial x}(\rho(\text{Ni}) * v(\text{Ni})) \quad (8)$$

$$\frac{\partial \rho(\text{Al}_2\text{O}_3)}{\partial t} = 2W_1(T)\mu(\text{Al}_2\text{O}_3) - \frac{\partial}{\partial x}(\rho(\text{Al}_2\text{O}_3) * v(\text{Al}_2\text{O}_3)) \quad (9)$$

$$\frac{\partial \rho(\text{O}_2)}{\partial t} = (W_0(T) - 3W_1(T))\mu(\text{O}_2) - \frac{\partial}{\partial x}(\rho(\text{O}_2) * v(\text{O}_2)) \quad (10).$$

Here the density of each element is the product of true density and volume ratio of its content. For incompressible media (except gas) these equations describe dynamics of volume ratio changes. The condensed components of *i-th* medium are supposed to be incompressible. Their volume ratio in the unit volume is characterized by v_i parameters, hence the density of *i-th* component in the

composition is $\rho_i = \rho_i^0 v_i$. For the gas component $v_g = 1 - \sum_i v_i$. The gas medium is assumed as ideal gas satisfying the equation $\rho_g = p\mu_g / RT_g$, where T_g is gas temperature, R is gas constant, p – pressure, μ_g – gas molecular mass. The laws of conservation of momentum for metal, ceramics, and oxidizing gas in conditions of a slow-velocity motion of the mixture medium compared with the speed of sound are reduced to the balance of the basic forces acting on the medium. For the metal group:

$$\rho_m \left(\frac{\partial \mathbf{v}_m}{\partial t} + \mathbf{v}_m \frac{\partial \mathbf{v}_m}{\partial x} \right) = \mathbf{0} = -\mathbf{v}_m \frac{\partial \rho}{\partial x} + \mathbf{v}_m \frac{\partial}{\partial x} \left(\eta_m \frac{\partial \mathbf{v}_m}{\partial x} \right) - f(L+x) \omega^2 \rho_m - \dots$$

$$\alpha_{11} v_m v_m + \alpha_{12} (v_c - v_m) + \alpha_{13} (v_g - v_m) + 2W_0 \mu(\text{Ni})(v_c - v_m) \quad (11)$$

For the metal component: the pressure gradient multiplied by the cross-sectional area (which is proportional to v_m) is balanced, first, by centrifugal forces affecting the metal components in the emulsion; secondly, by the forces of viscous interaction with other components of the emulsion under their relative motion, and also by the exchange of momentum during chemical mass transfer. Similar equations are valid for ceramics and gas.

$$\rho_c \left(\frac{\partial \mathbf{v}_c}{\partial t} + \mathbf{v}_c \frac{\partial \mathbf{v}_c}{\partial x} \right) = \mathbf{0} = -v_c \frac{\partial \rho}{\partial x} + v_c \frac{\partial}{\partial x} \left(\eta_c \frac{\partial \mathbf{v}_c}{\partial x} \right) - f(L+x) \omega^2 \rho_c - \dots$$

$$\alpha_{22} v_c v_c + \alpha_{21} (v_m - v_c) + \alpha_{23} (v_g - v_c) + W_1 (4\mu(\text{Al})(v_m - v_c) + 3\mu(\text{O}_2)(v_g - v_c)) \quad (12)$$

$$\rho_g \left(\frac{\partial \mathbf{v}_g}{\partial t} + \mathbf{v}_g \frac{\partial \mathbf{v}_g}{\partial x} \right) = \mathbf{0} = -\mathbf{v}_g \frac{\partial \rho}{\partial x} + \mathbf{v}_g \frac{\partial}{\partial x} \left(\boldsymbol{\eta}_g \frac{\partial \mathbf{v}_g}{\partial x} \right) - f(L+x) \omega^2 \rho_g - \dots$$

$$\alpha_{33} v_g v_g + \alpha_{13} (v_m - v_g) + \alpha_{23} (v_c - v_g) + W_0 \mu(\text{O}_2) (v_c - v_g) \quad (13)$$

Here L is the distance from the centrifuge axis to the exposed surface of the reactor; f is a multiplier; η – viscosity, ω – angular velocity of centrifugal action on the components of the emulsion; α_{ii} , α_{ij} , α_{ji} – coefficients of viscous interaction forces (i, j vary from 1 to 3).

The laws of conservation of energy are characterized by the equations of thermal conductivity for three groups (metal, ceramics and gas) with due regard of the mobility of the emulsion components and heat exchange between the groups and the external environment (its temperature is assumed to be constant equal to the initial T_0). As the main sources of heat release, we take into account the exothermicity of the chemical interaction in the group, the energy exchange caused by the mass transfer between the groups during the chemical reaction. We neglect the less significant sources and confine ourselves to a one-dimensional description in order to simplify (describe) and analyze the results obtained. Below we give, for brevity, only the equation for the group of metals, the other equations are similar:

$$c_m \rho_m \left(\frac{\partial T_m}{\partial t} + v_m \frac{\partial T_m}{\partial x} \right) = \frac{\partial}{\partial x} \left(\lambda_m \frac{\partial T_m}{\partial x} \right) + (\overline{QW})_m + 2(c\mu)_{Ni} W_0 (T_c - T_m) - \alpha_{mc} (T_m - T_c) - \alpha_{mg} (T_m - T_g) - \alpha_{mw} (T_m - T_0). \quad (14)$$

Here $(\overline{QW})_m = Q_{Al} W_1 \mu_{Al} + Q_{NiAl} W_2 \mu_{NiAl}$. The coefficients α_{mc} , α_{mg} , α_{mw} characterize the heat exchange between the components of the emulsion.

The initial conditions: $T_m = T_c = T_g = T_0$.

Boundary conditions at the ends: $T_m(0, t) = T_c(0, t) = T_g(0, t) = T_W$ – the condition for initiating the combustion process (they can be of the impulse type);

$$\left(\frac{\partial T_m}{\partial x}\right)_{(l,t)} = \left(\frac{\partial T_c}{\partial x}\right)_{(l,t)} = \left(\frac{\partial T_g}{\partial x}\right)_{(l,t)} = 0 \quad \text{– adiabaticity condition at the closed}$$

(bottom) end.

RESULTS OF ANALYSIS

The results of numerical simulation of the combustion process dynamics are presented on the space-time charts of temperature, specific fraction of chemical reagents and rates of their convective transfer. The process is initiated by a high-temperature source (spiral) from the open end of the reactor ($x = 0$). The frontal process of the exothermic chemical interaction of the mixture is formed. In Fig. 1 we see successive distributions (from left to right) of the gas, ceramic and metal temperature fields through a constant time interval. These distributions prove that a high-temperature region expanding to the right is formed. The structure of the right edge of this region (front zone) stabilizes its characteristics. In reality, they are slowly changed (due to the centrifugal forces and mobility of the combustion products), so the front is called quasi-stationary. The initial stage of formation (the stage of ignition) is noticeable against the background of steady burning. At this stage, an excess of enthalpy appears in the front structure, which moves along with the front. It plays an important role in the analysis of its stability and affects the distribution of the temperature of the medium when the front reaches the bottom of

the reactor (neighborhood $x = 20$). The determining role in the combustion process of the mixture medium is played by the exothermic transformation in the metallic phase. Through heat exchange, it involves the ceramic and gas "phases" that determine the uniform structure of the combustion front of the mixture medium. It should be underlined that the features of the temperature distribution of ceramics and gas are explained not only by the classical conductive heat exchange, but also by the energy exchange caused by interfacial mass transfer. Under the terms of adiabatic steady-state combustion (in Figure 1, the mixture medium burns in the absence of heat exchange with the external environment), the adiabatic combustion temperature is established behind the combustion front in the products. In this case it can be seen that in the metallic phase, superadiabatic temperatures are reached in the reaction zone. It enables an increase in the propagation velocity of the front, which is shown in Fig. 2. The figure demonstrates the quasistationary character of the combustion front propagation due to the influence of the varying field of centrifugal forces. The field depends on the redistribution of the reagents mass within the exothermic chemical interaction the dynamics of which is shown in Fig. 3 and Fig. 4. Here, like Fig. 1, the space-time distributions (at the same moments as the temperature fields) of the specific volumes of the chemical reagents of the mixture during its burning are presented. We see how the composition of the mixture changes within the front propagation due to chemical interaction and convective transfer of the melt under the action of centrifugal forces. Convective transport is represented by the space-time distribution of the velocity fields in Fig.

5. At the stage of ignition (small x), we see negative values of the velocity of the medium; it corresponds to the experimentally observed spread of the medium. Later, the melt moves due to the processes of densification of a gas-saturated medium due to the action of centrifugal forces.

With intensive heat exchange between the components, the temperature fields of the metal, ceramics and gas differ slightly. We have a one-temperature description of the combustion process (gasless or filtration combustion mode). Under the conditions of the flat combustion front instability (large excess of enthalpy, relatively low combustion temperatures), combustion is observed in the alternating mode. The distribution of the temperature fields is shown in Fig.6. The quasistationary effect of centrifugal forces changes the period and amplitude of the oscillations. It is a quasi-stationary analog of the pulsating combustion mode [4].

CONCLUSIONS

A mathematical model of combustion of a mixture composition under the action of centrifugal forces was proposed and analyzed. It takes into account the temperature and phase inhomogeneity of the combustion products in the form of a melt. The liquid state of the multicomponent suspension with different component densities under the terms of centrifugal action forms a multi-velocity mixture medium and phase separation in it. A more complete description of the exothermic chemical interaction expands the regulation possibilities of the SHS technology under extreme conditions.

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REFERENCES

1. Levashov E.A., Rogachev A.S., Kurbatkina V.V., Maksimov Yu.M., Yukhvid V.I. Promising materials and technologies of self-propagating high-temperature synthesis, -M.: Publ.House MISIS, 2011
2. Nigmatulin R.I. Dynamics of multiphase media, -M.: Nauka, Fiz-mat lit., 1987, 1.
3. Frank-Kamenetsky D.A. Diffusion and heat transfer in chemical kinetics, -M.: Nauka. 1987.
4. Shkadinsky K.G. Khaikin B.I., Merzhanov A.G. Propagation of pulsating front of exothermic reaction in condensed phase. Fizika gorennya i vzryva. 1971, v.7, No.1, p.19-28.

CAPTIONS

Fig. 1. Consecutive distributions (from left to right) of the gas, ceramic and metal temperature fields with a constant time interval.

Fig. 2. Quasi-stationary mode of combustion front propagation due to varying field of centrifugal forces (1 – $w = 10, L = 10$; 2 – $w = 20, L = 10$; 3 – $w = 30, L = 5$; 4 – $w = 30, L = 10$).

Fig. 3. Space-time distribution (at the same moments as temperature fields) of metal specific volume in combustion process.

Fig. 4. Space-time distribution (at the same moments as temperature fields) of ceramics specific volume in combustion process.

Fig. 5. Space-time distribution of gas, ceramics and metal velocity fields.

Fig. 6. Temperature field distribution in alternating mode. ($w = 10, L_n = 10$ (1) $w = 20, L_n = 10$ (2); $w = 30, L_n = 5$ (3) $w = 30, L_n = 10$ (4)).

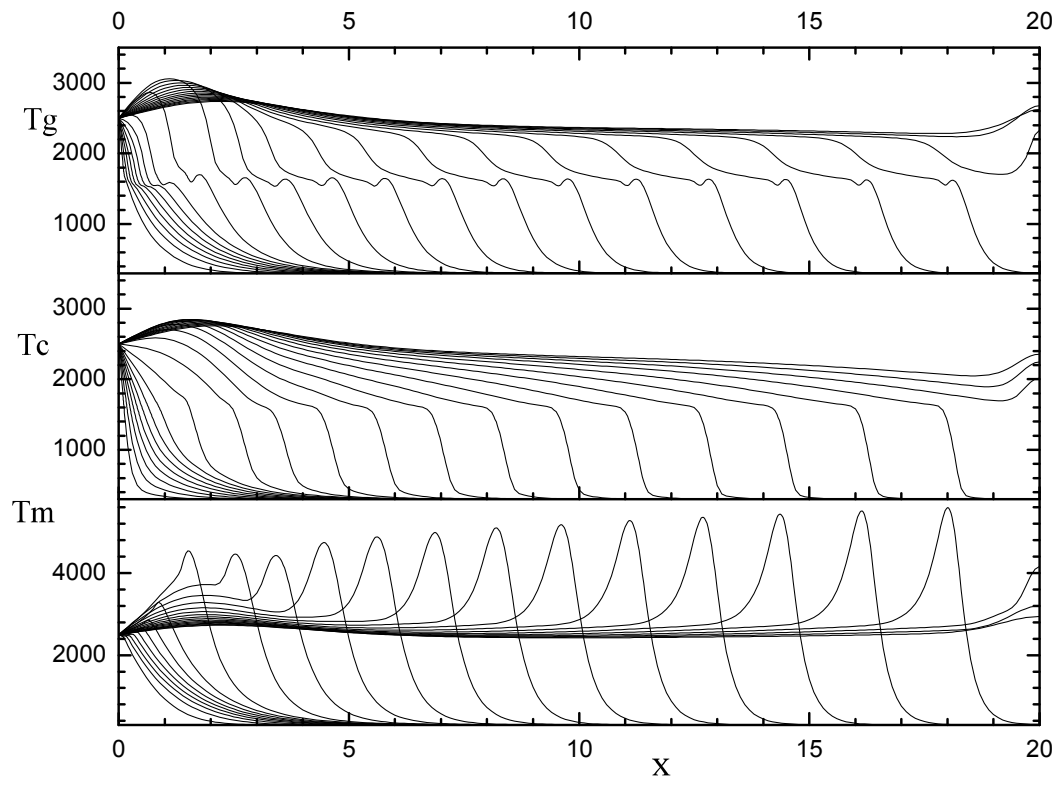


Fig. 1.

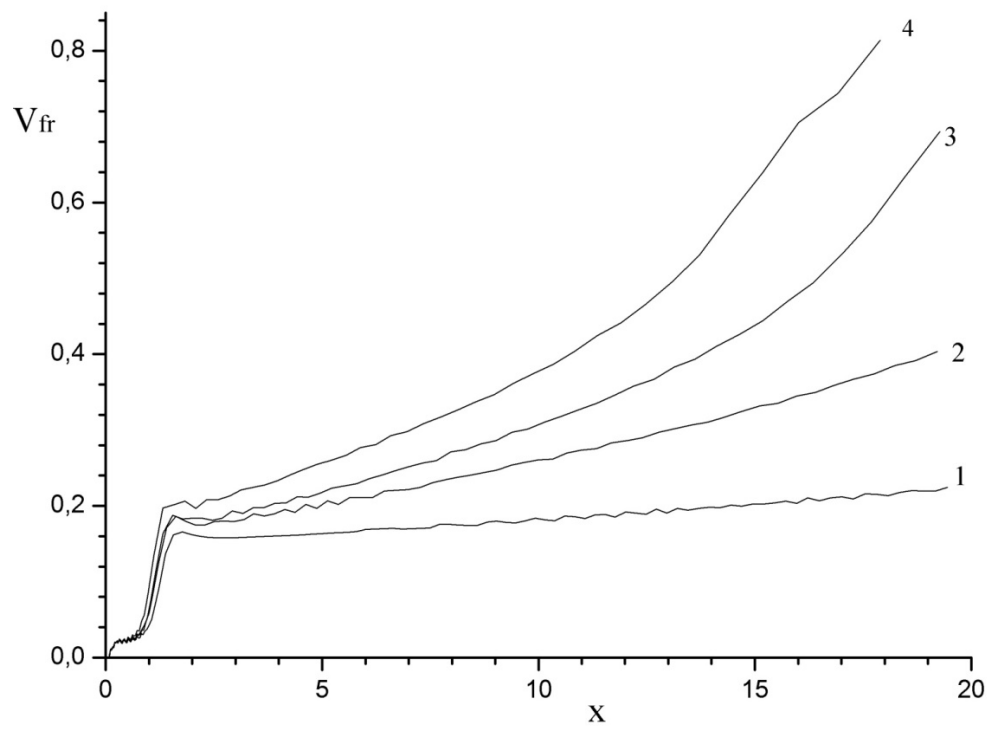


Fig. 2.

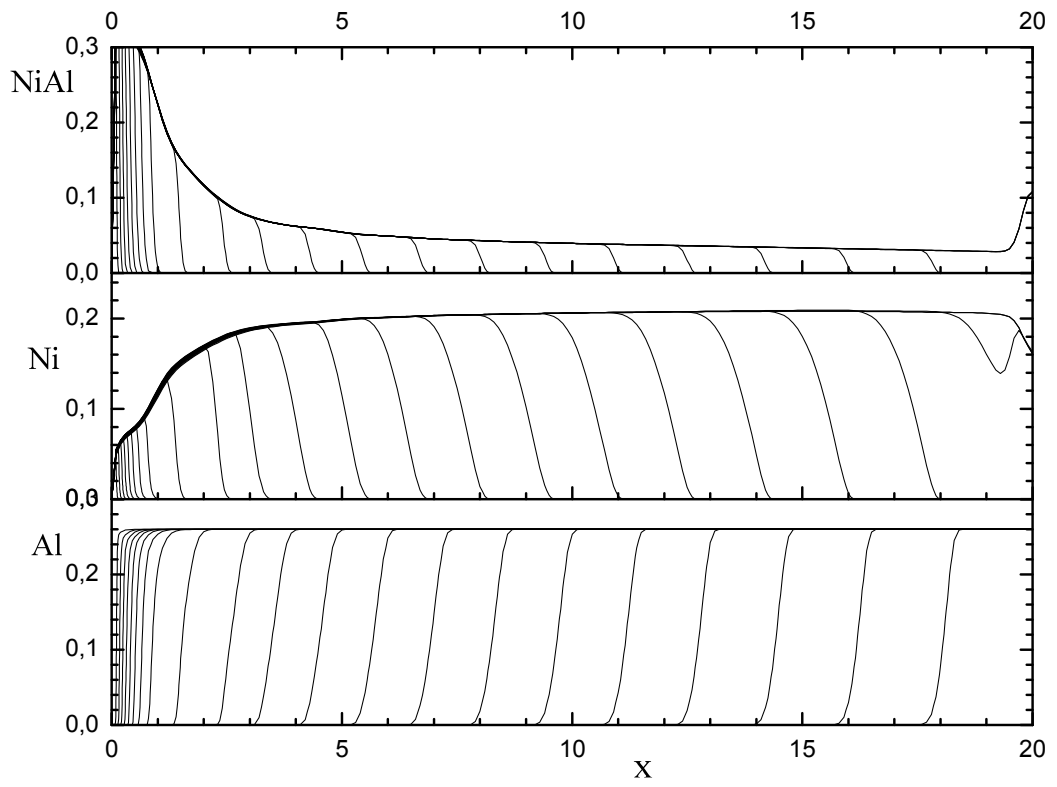


Fig. 3.

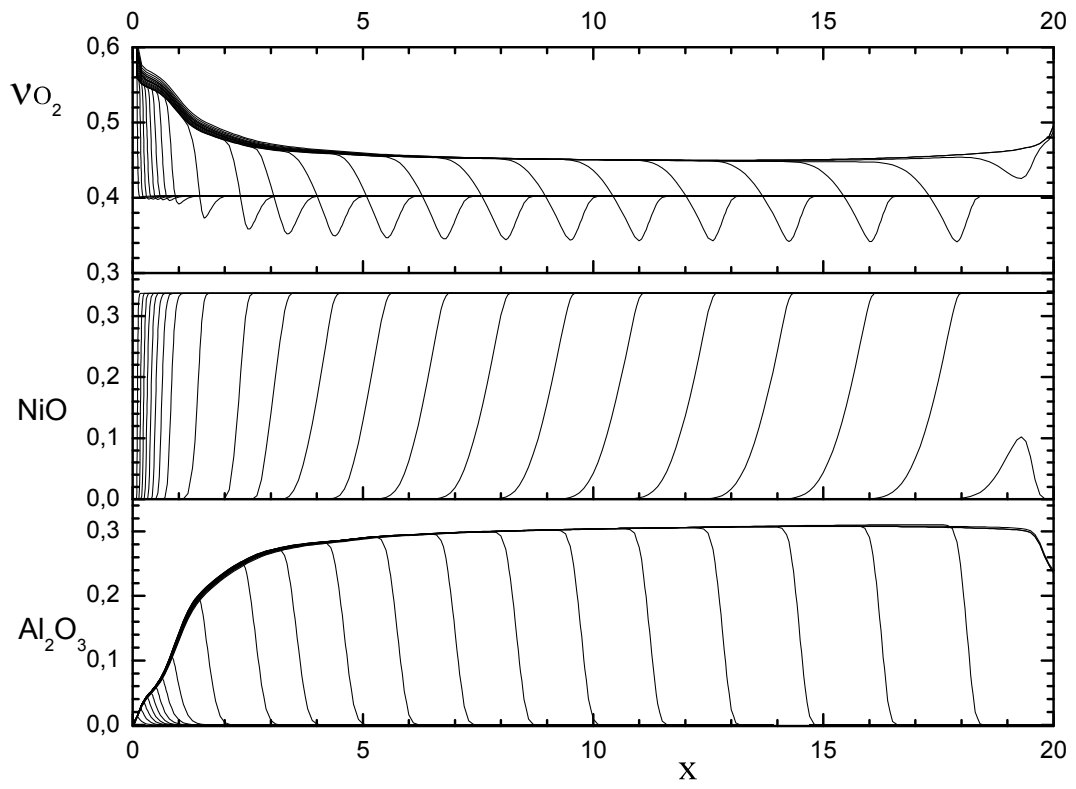


Fig. 4.

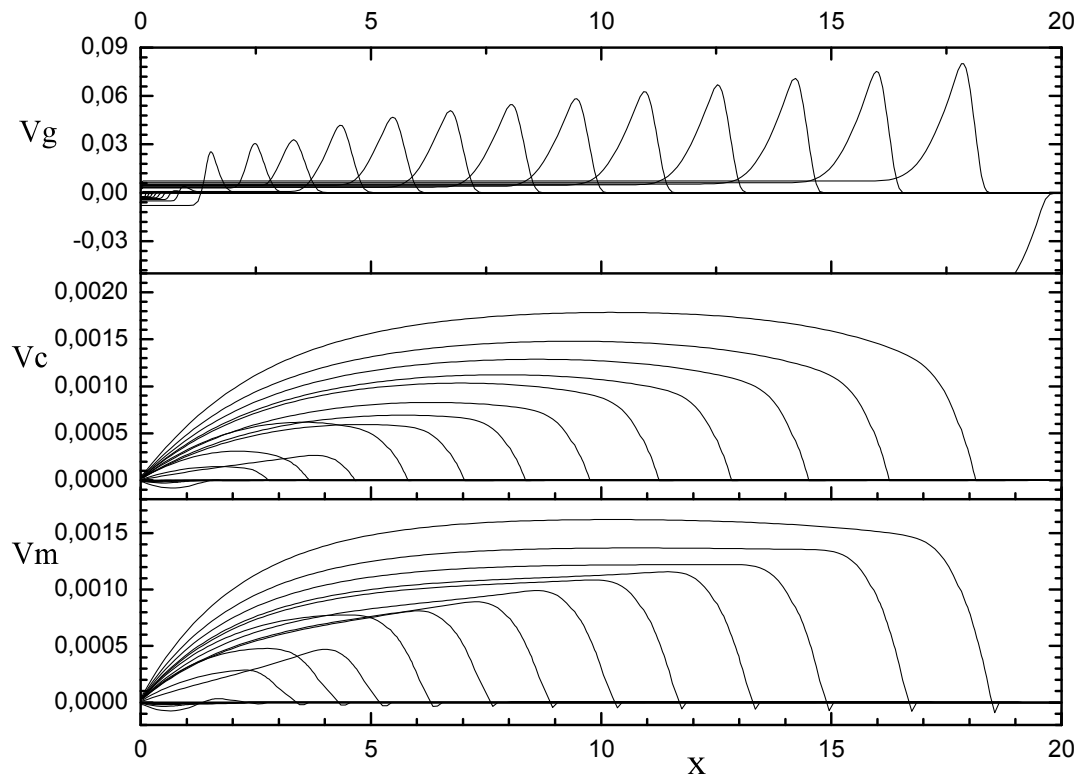


Fig. 5.

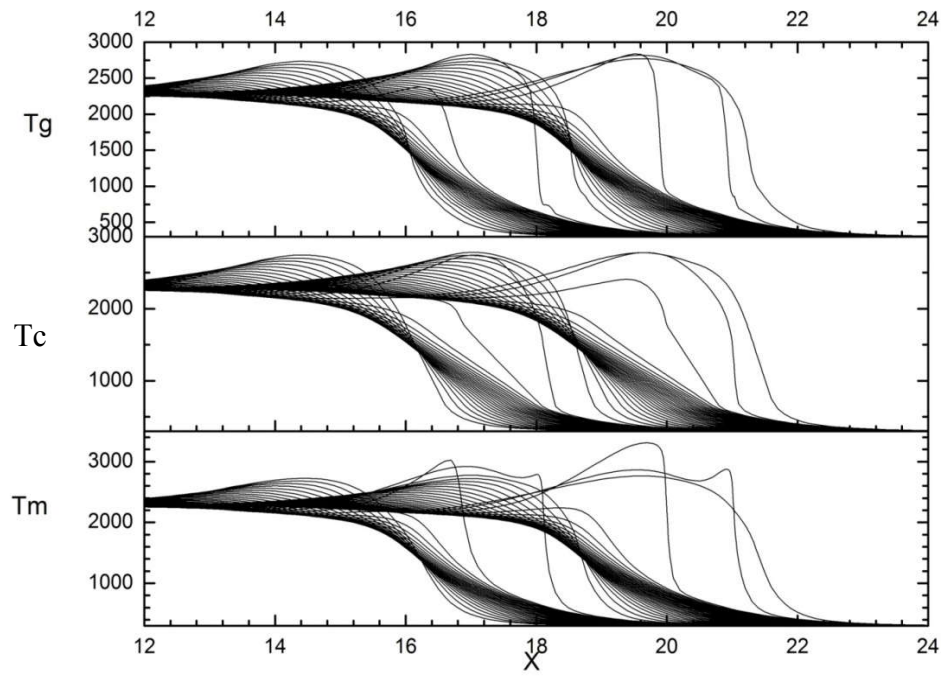


Fig. 6.