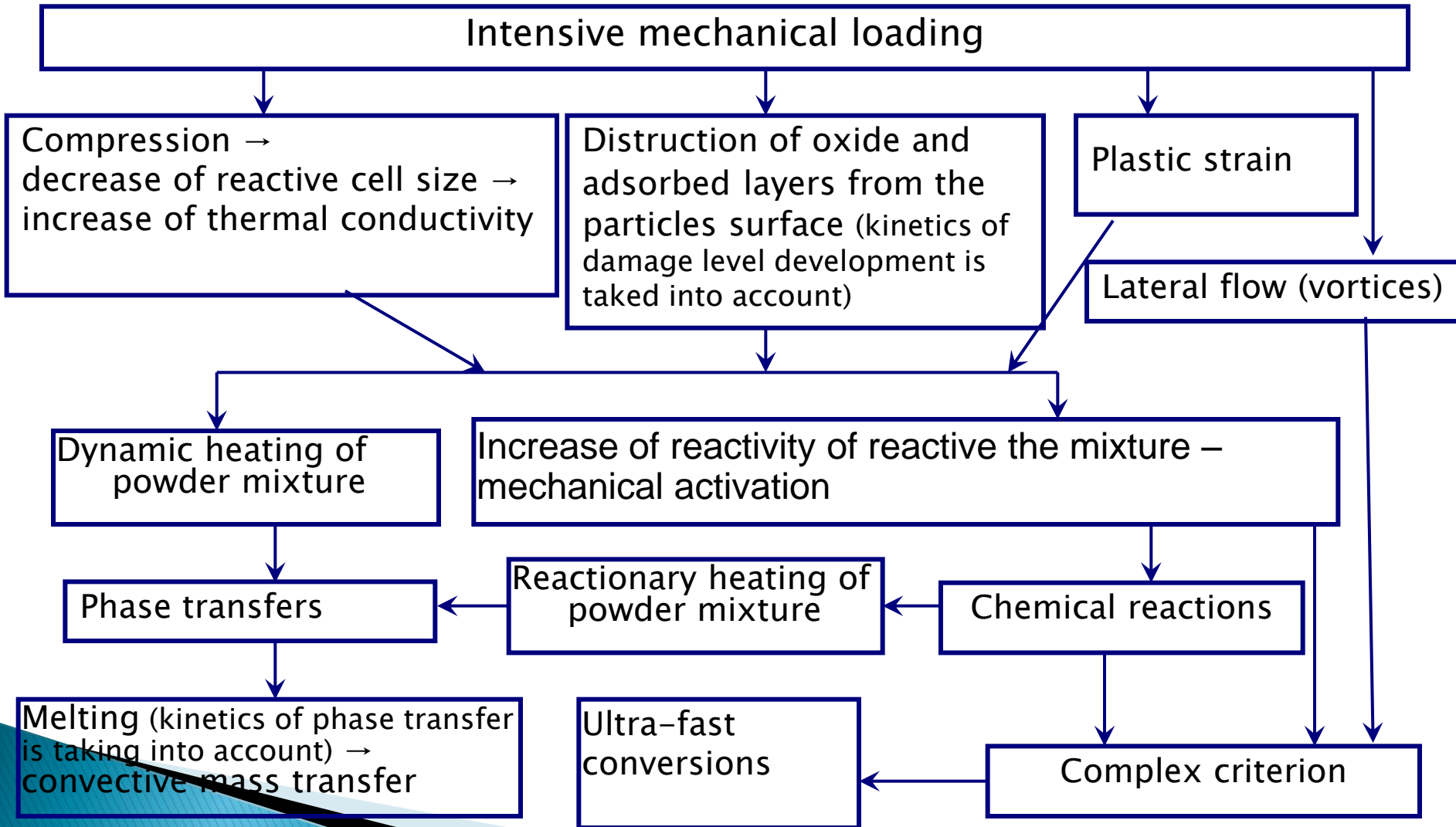




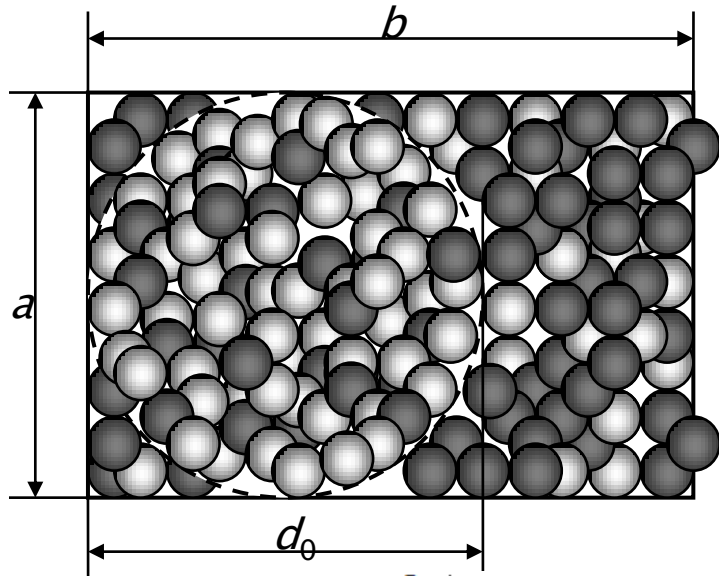
Computer Simulation of Reactive System Dynamics

Maria A. Dmitrieva, Vladimir N. Leitsin

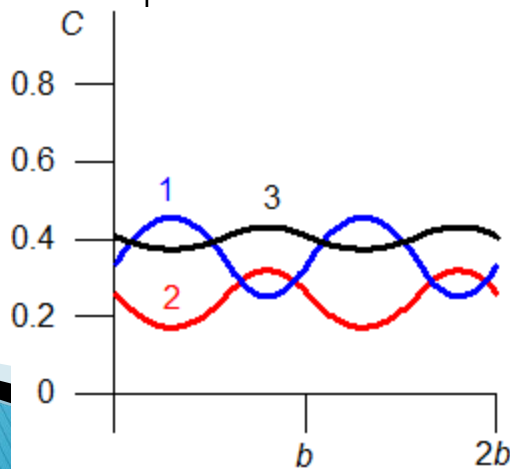
Computer Simulation Concept



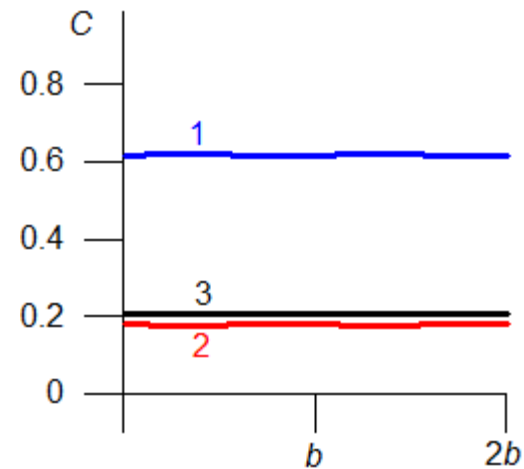
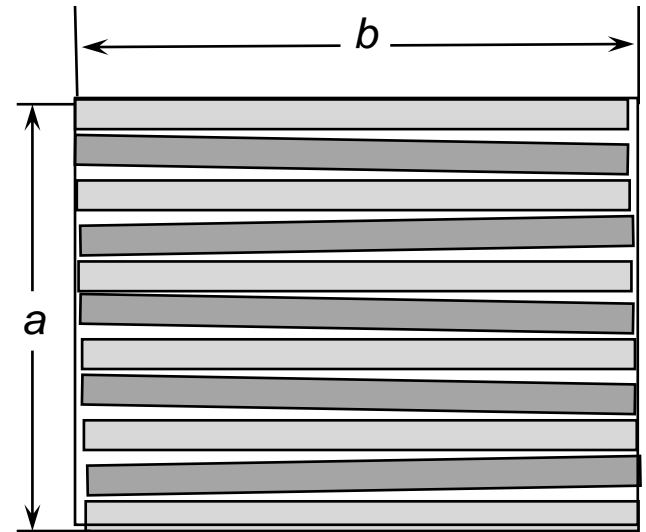
Powder system structure



Reactive cell



Multilayer system structure



State parameters of powder medium behind shock pulse front

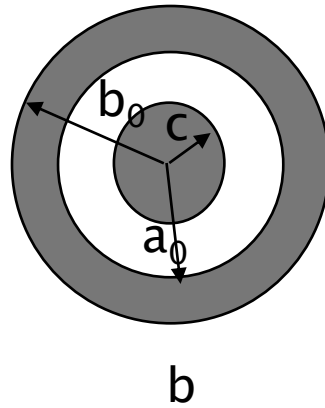
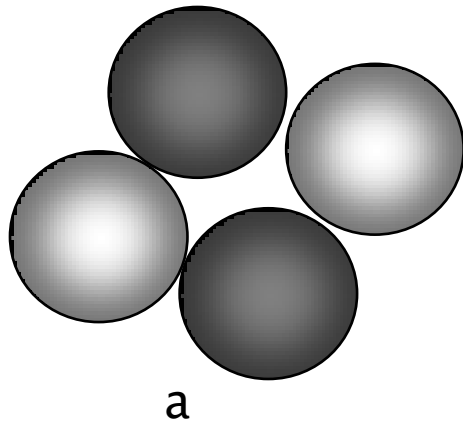
$$U_f = v_{imp} + [a_f + (1 - \Pi)D_p] / 2b_f + \\ + \{ [a_f + (1 - \Pi)D_p]^2 / 4b_f^2 + (1 - \Pi)v_{imp}D_p / b_f \}^{1/2},$$

$$P_f = (1 - \Pi_0)\rho_0 D_p U_f,$$

$$\rho_f = (1 - \Pi)\rho_0 D_p / (D_p - U_f), \quad W = U_f^2 / 2,$$

$$1/D_p = (1 - \Pi) / (a_f + 0.5b_f v_{imp}) + \Pi / v_{imp}$$

The porous medium is simulated by a modified Nesterenko single-pore model with a nondeformable central core



$$a_0 = \frac{d}{2} \quad b_0 = \frac{d}{2} \sqrt[3]{\frac{1}{1-\Pi_0}};$$

$$c = \frac{d}{2} \sqrt[3]{2 - \frac{1}{1-\Pi_0}}.$$

Real material (a), Nesterenko model (b)

specific energy, W_D , dissipating in the surroundings of a pore at the collapse stage

$$W_D = \frac{2\sigma_T}{3\rho_s} |H(x_0) - H(x_1)|, \quad H(x) = \ln x - 1,$$

$$x_0 = \frac{1}{\Pi_0}; \quad x_1 = \frac{1 - \Pi_0}{(1 - \Pi_1)\Pi_0};$$

at further stages, energy is expended to disrupt the boundary layers of particles implementing non-stationary compacting mode mechanisms

$$W_k = W - W_D$$

The mechanical loading of powder mixture can increase the reactionary ability of reactive components

1. Plastic deformation:

$$P_{sl} = P_{\min} = \frac{2}{3} \sigma_T \ln \left(\frac{\rho_s}{\rho_s - \rho_0} \right),$$

$$A_1 = \sum_{i=1}^N \sigma_{Ti} \theta_i m_i / \rho_i;$$

2. Fracture of surface layers:

$$P_{s2} = 0,36 \frac{\rho_0}{\rho_s} \frac{Hv}{(1 - \rho_0/\rho)},$$

$$A_2 = \sum_{i=1}^N W_{bi} m_i / \rho_i;$$

Dynamic model of fracture

The instantaneous damage ω_0 as a function of applied pressure p can be written [1] in the form:

$$\omega_0 = \frac{p^2}{\sigma_B^2},$$

σ_B - is the breaking point of a powder component

- Further development of material fracture is defined by the incubation period τ [2]:

$$\tau = \frac{2 K_{Ic}^2}{\pi \sigma_B^2 c}$$

K_{Ic} - is the fracture toughness and c is the velocity of elastic waves

- A criterion for complete fracture of material

$$\omega \Big|_{t=\tau} = 1.$$

- The kinetic equation of material damage

$$\frac{d\omega}{dt} = \frac{1 - \omega_0}{\tau - t_0}.$$

[1] Kashtanov, A.V. and Petrov, Yu.V., Tech. Phys., 2006, vol. 51, no. 5, pp. 604-614.

[2] Glebovskii, P.A. and Petrov, Yu.V., Phys. Solid State, 2004, vol. 46, no 6, pp. 1051-1054.

The law of conservation of energy

$$(1 - \Pi_l) \frac{\partial(\rho_s c_s T_s)}{\partial t} + \alpha_v f_T (T_s - T_l) = \frac{\partial}{\partial x} \left[\lambda_s (1 - \Pi_l) \frac{\partial T_s}{\partial x} \right] + q_{v+} + q_{v-},$$

$$\Pi_l \frac{\partial(\rho_l c_l T_l)}{\partial t} - \alpha_v f_T (T_s - T_l) = \frac{\partial}{\partial x} \left[\lambda_l \Pi_l \frac{\partial T_l}{\partial x} \right] - c_l \rho_l v \frac{\partial T_l}{\partial x},$$

$$t = 0, T_l = T_s = T(x),$$

$$x = 0, T_s = T_l = T_f, \quad x = nb, \frac{\partial T_s}{\partial x} = \frac{\partial T_l}{\partial x} = 0.$$

Heat sources:

$$q_{v+} = \gamma_i \frac{\partial A_i}{\partial t} + \frac{\partial z}{\partial t} Q$$

Heat losses:

$$q_{v-} = \begin{cases} \frac{\partial \omega_m}{\partial t} Q_i, & T_s = T_p^i \\ 0, & T_s \neq T_p^i \end{cases} \quad \omega_m = \frac{t - t_{m0}}{\tau_m - t_{m0}},$$

$$\tau_m = 0,7 \mu s$$

The exothermal conversion macrokinetics is supposed to be a multilevel reactionary cell model coordinated with the power law of reactionary diffusion

$$\frac{\partial z}{\partial t} = k_0 \exp(-E_a / RT) \varphi(z),$$

$\varphi(z) = (1 - z)^{m-1/n}$, The kinetic function $\phi(z) = 0,5 z^{-1}$

Pre-exponent $k_0 = k / b^{n+1}$,

$E_a = E_0 - H(P - P_i^*) \alpha_i A_i$, Change in the reactivity

Condition of reactive equivalence $\beta = \frac{E_a}{RT} = \frac{E_0}{RT_0} = B,$

Filtration of liquid phase obeys the Darcy law

$$\nabla P_{\text{жс}} = \left(-\frac{\mu}{K} \right) v,$$

$$\nabla v = 0,$$

Permeability coefficient

$$K = \Pi^2 d^2 / 180(1 - \Pi)^2,$$

Viscosity of the melt

$$\mu = \mu_0 \exp(E_\mu / RT),$$

$$P_{\text{жс}} = P_{tk} + P_{\text{жсф}},$$

Porous pressure

$$P_{tk} = [C_b \alpha_b - (C_a \alpha_a + \Pi)] \frac{(T - T_{nl})}{1 - 2\nu} E,$$

$$P_{\text{жсф}} = P_f - C_a \sigma_T(T).$$

A necessary condition for ultra-fast transformations at the initial stage of synthesis is the emergence of cross-flows

$$\left(\frac{D \dot{D}}{u \dot{u}} \right) = 1, \quad \text{Mescheryakov's statistical criterion}^1$$

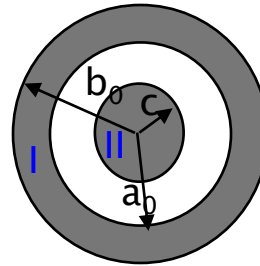
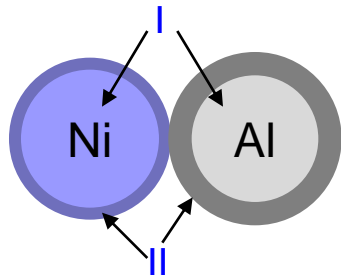
$$z \leq z_m, \quad \frac{E_a}{RT} \leq \frac{E_{a0}}{RT_0}, \quad \text{The achievement of the required degree of mechanical activation}$$

$$\Pi \geq \Pi_{\min}, \quad \varepsilon \geq \varepsilon_s.$$

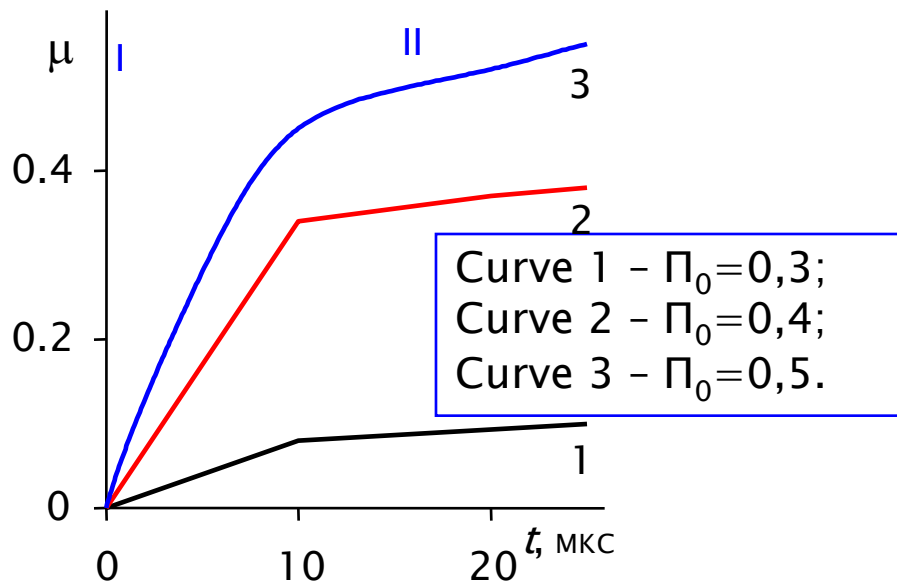
The fulfilment of non-stationary criterion results in the wave flow of medium characterised by the loss of mass velocity in the shock pulse direction. Cross-flows ensure the convective transport of components in the microvolumes of reactive mixture, thus the non-stationarity criterion determines one of the necessary conditions for the formation of the substructure of synthesis product as well as for the opportunity for the implementation of ultrafast chemical transformations on the rising edge of shock impulse.

¹Mescheryakov Yu. I. // Control in Physicotechnical Systems, Fradkov, A.L., Ed., St. Petersburg: Nauka, 2004, pp. 222-245.

The non-uniformity of particles plastic deformation



$$\Delta r = \frac{d}{2} \left(1 - \sqrt[3]{2 - \frac{1}{1 - \Pi}} \right)$$

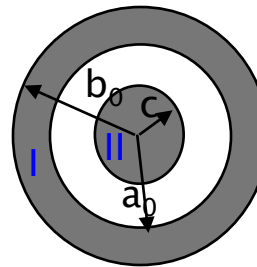
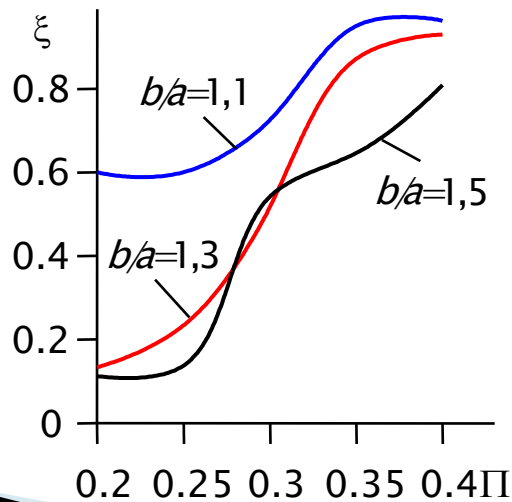
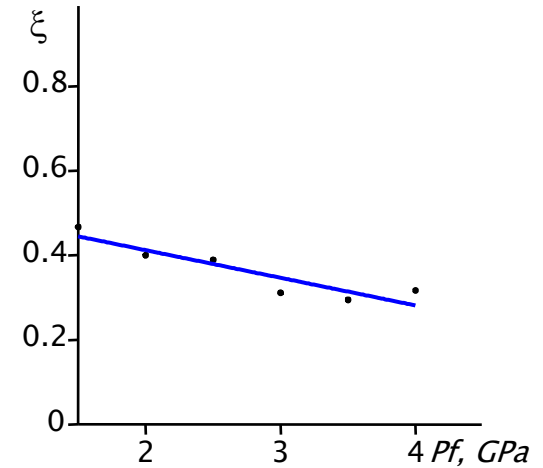
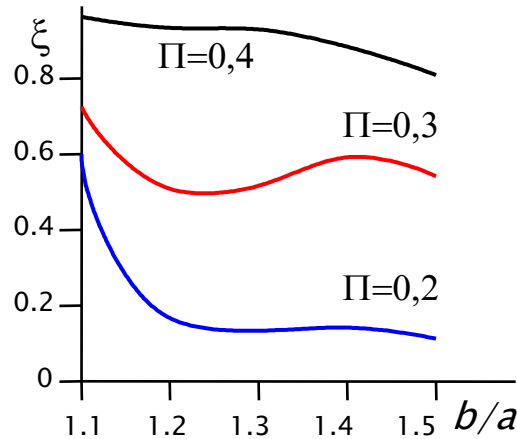
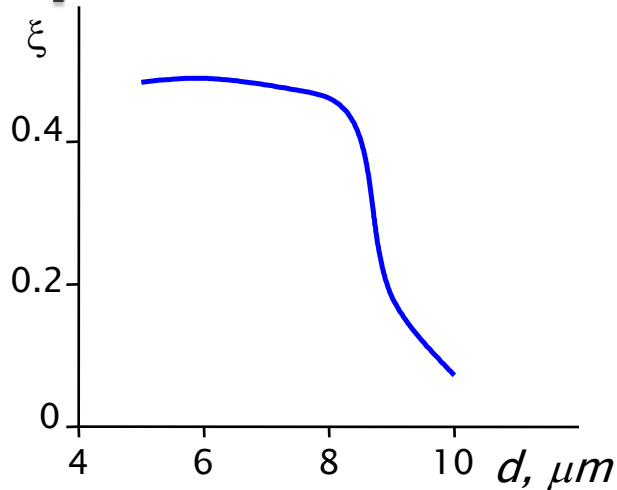


At a low intensity of dynamic impact or low porosity, the thermal effect of shock-induced chemical transformations will not cause particle heating in this layer, which is necessary for the thermal initiation of reaction in the non-deformed parts of reactive components. The product of mechanochemical transformations will be a composite consisting of the structural elements of initial mixture components and the reaction product.



$$b/a = 1,5; \Pi_0 = 0,3 \div 0,5; d_{\text{Ni}} = d_{\text{Al}} = 5 \text{ мкм}; T_0 = 293 \text{ K}; P_f = 2 \text{ ГПа}; t_{\text{imp}} = 1 \text{ мкс}$$

Relative volume of zones of possible ultrafast transformations



$$\left(\frac{D \dot{D}}{u \dot{u}} \right) = 1,$$

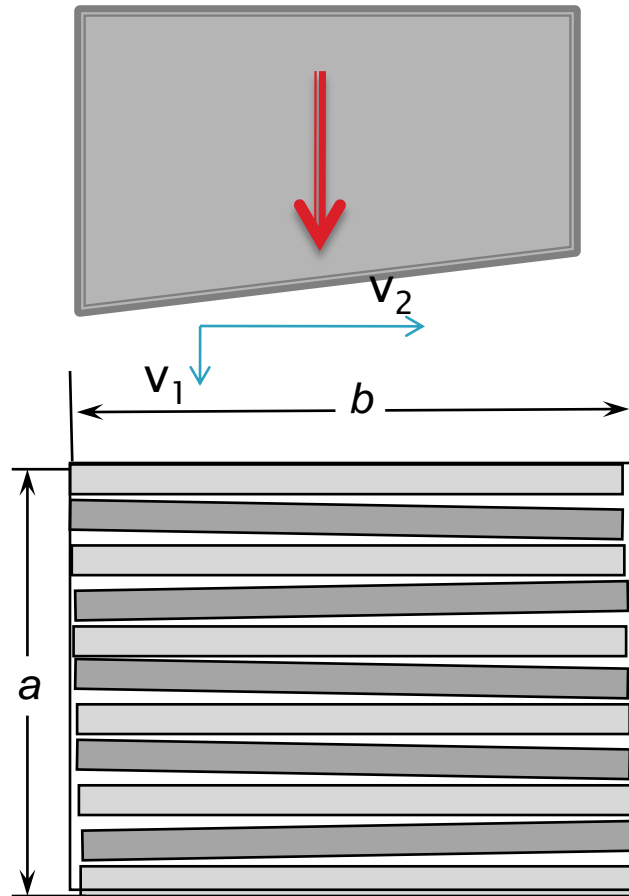
$$z \leq z_m, \quad \frac{E_a}{RT} \leq \frac{E_{a0}}{RT_0},$$

$$\Pi \geq \Pi_{\min}, \quad \varepsilon \geq \varepsilon_s.$$

Ni + 31,5 мас. % Al = NiAl + Q

$b/a = 1,1 \div 1,5$; $\Pi_0 = 0,2 \div 0,4$; $d_{Ni} = d_{Al} = 4 \div 10 \mu\text{m}$;
 $T_0 = 293 \text{ K}$; $P_f = 1 \div 4 \text{ GPa}$; $t_{imp} = 1 \mu\text{sec}$

Simulation of processes in layered systems



Natural vibration frequencies

Rayleigh wave velocity

$$R(c)=0,$$

$$R(c) = (2 - m_2^2)^2 - 4\sqrt{1 - m_1^2} \sqrt{1 - m_2^2},$$

$$m_1 = c / c_1, \quad m_2 = c / c_2,$$

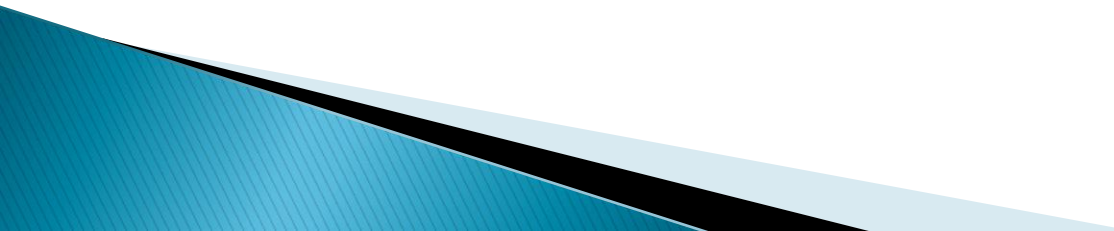
$$c_1 = \left[\frac{E(1 - \mu)}{\rho(1 + \mu)(1 - 2\mu)} \right]^{1/2},$$

$$c_2 = \left[\frac{E}{2\rho(1 + \mu)} \right]^{1/2}.$$

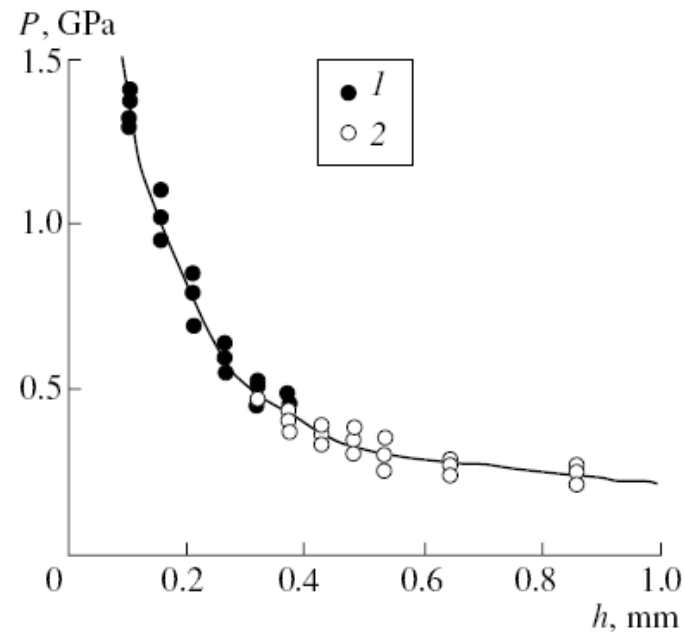
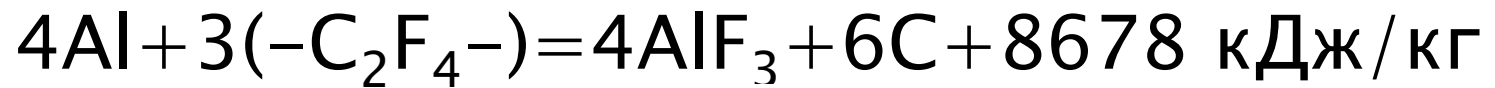
$$\omega_{ij} = \alpha_j^2 h_i \sqrt{\frac{E_i}{12\rho_i(1 - \mu_i^2)}},$$

$$\alpha^2 = m^2 \pi^2 / a^2 + n^2 \pi^2 / b^2$$

Investigation plan

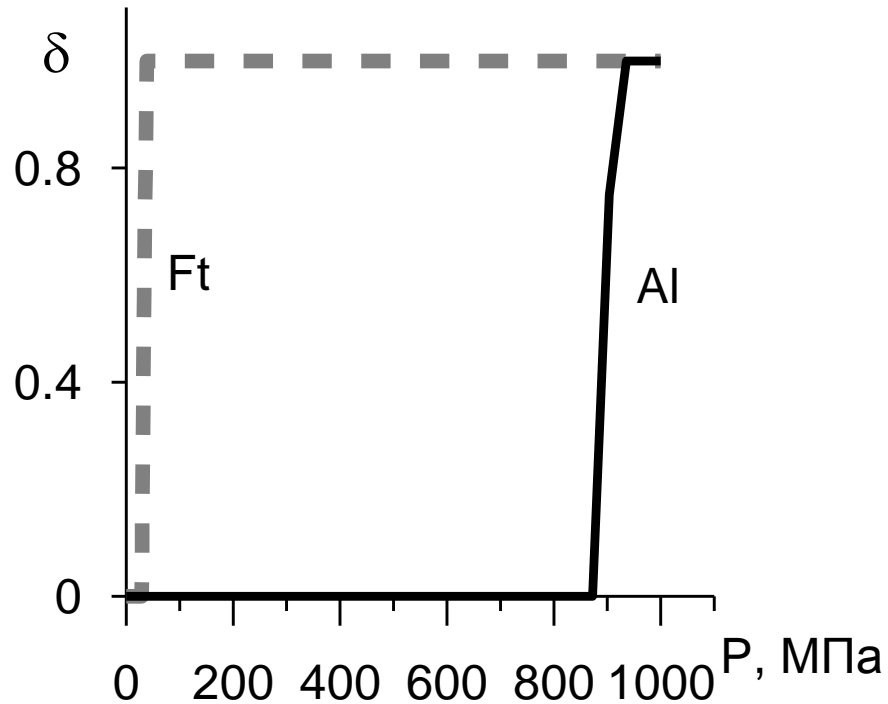
1. Determination of Rayleigh velocity of components;
 2. . Determination of the velocity of applied load;
 3. Determination of natural frequencies of the elements;
 4. Estimation of possible characteristic size of the texture of damaged material;
 5. Estimation of energy balance during the process of shock modification, taking into account the incubation time of damage;
 6. Estimation of local parameters of the kinetics of chemical reactions;
 7. Estimation of chemical transformations conditions .
- 

Initiation of reaction in thin-film samples



- ▶ Денисаев А.А., Штейнберг А.С., Берлин А.А. Иницирование реакции в тонкопленочных многослойных образцах алюминий-фторопласт при ударе на копре // Химическая физика. 2008. Т.27, № 6. С. 85–92

Simulation results



Dependence of the relative volume of the material δ , which reached the state of resonance on amplitude of the dynamic loading P

The results indicate the presence of a critical value of the amplitude of the shock pulse, the overcoming of which leads to a resonant mode at first in teflon ($P = 40$ MPa) and then in aluminum ($P = 880$ MPa).

Conclusion

- ▶ In case of ultradispersed powder reactive materials, the areas of non-stationary condition of dynamic compression are the most probable areas of the nanostructure formation. The analysis of the incubating times of powder component modification makes it possible to apply the model to the shock synthesis of composite materials.
- ▶ The powder material structure behind the shock pulse front is determined by initial structure of reactive compact – particles size, average porosity and concentration inhomogeneity degree. The relative volume of ultrafast reaction areas practically does not depend on the amplitude of the dynamic loading. There are practically significant variation ranges of concentration inhomogeneity degree and particles size. Within these ranges realization of physico-chemical transformations at the shock pulse front is possible.
- ▶ There is a threshold value of initial porosity, the excess of which results in a sharp increase in the concentration of zones of non-stationarity mode of dynamic compaction on the rising edge of shock pulse.

Thank You for Your attention