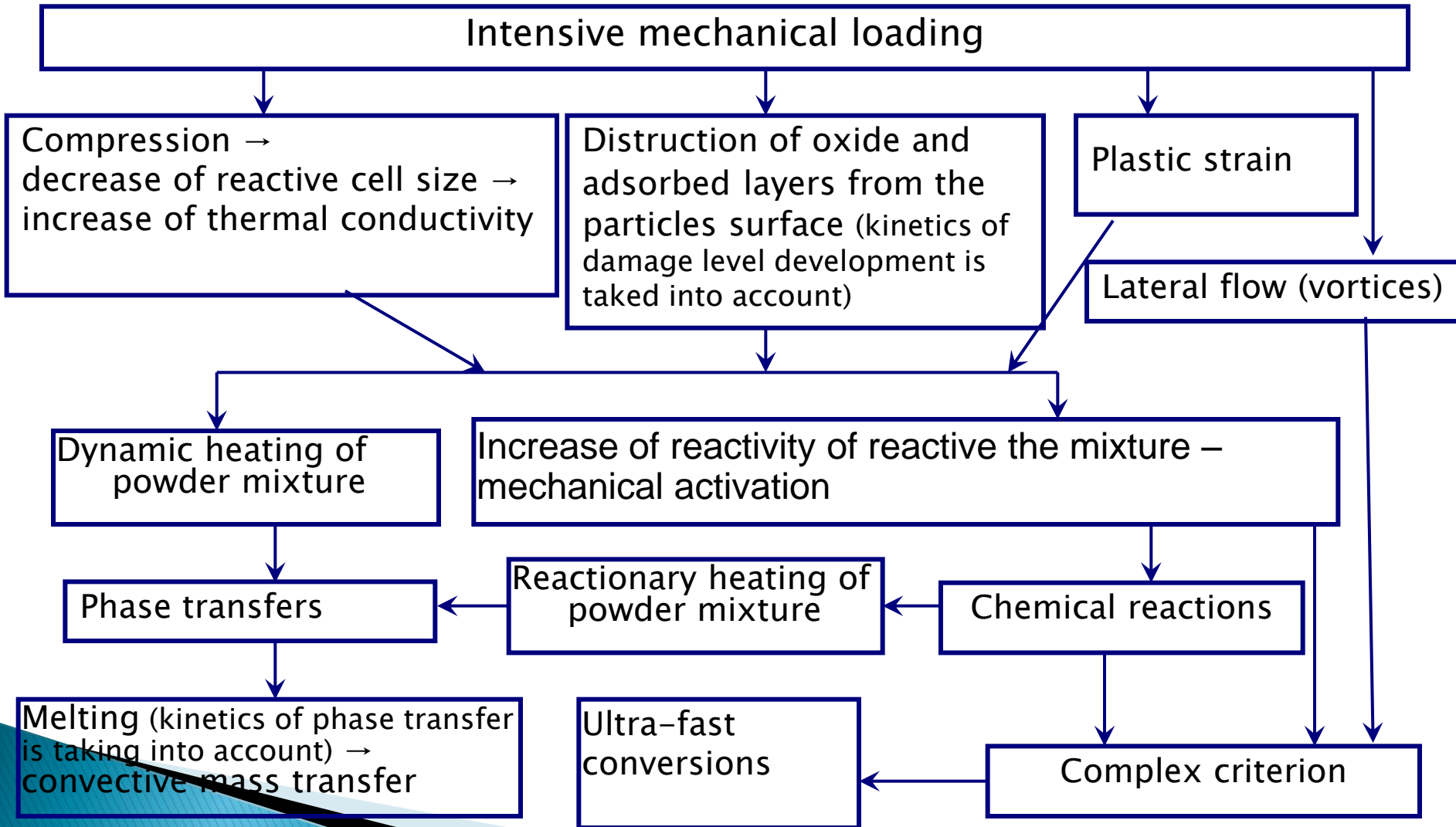




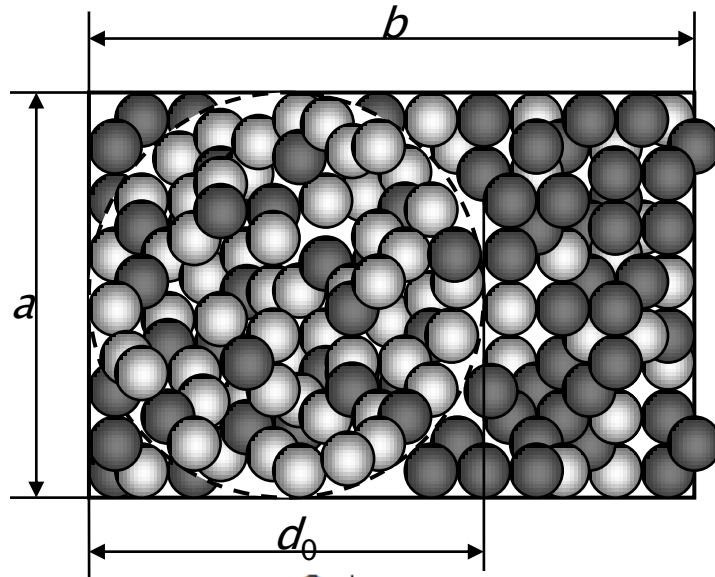
THE KEY FEATURES OF ZIRCONIUM DIBORIDE SHOCK SYNTHESIS

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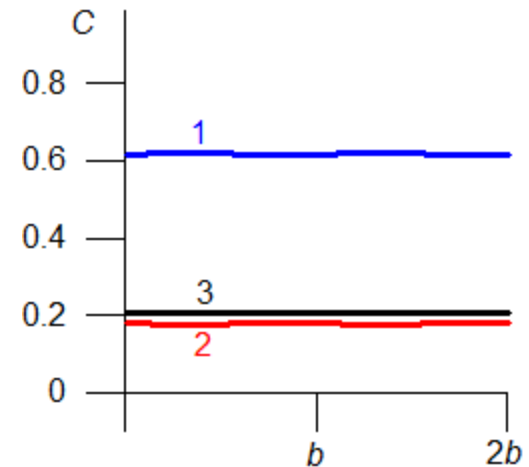
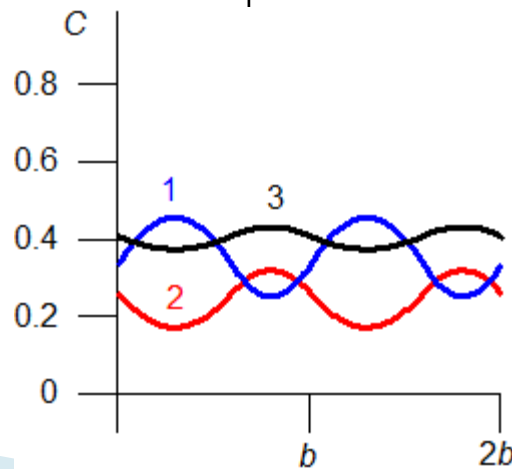
Computer Simulation Concept



Powder system structure



Reactive cell



State parameters of powder medium behind shock pulse front

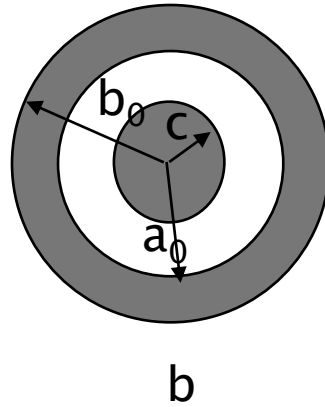
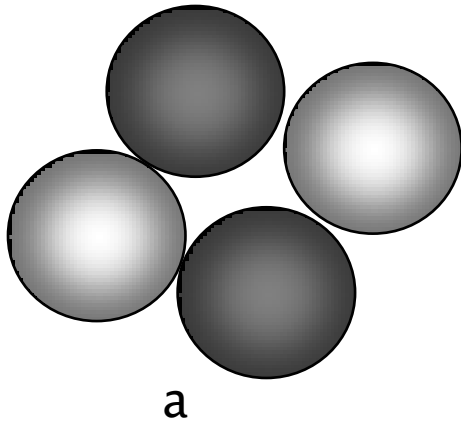
$$U_f = v_{imp} + [a_f + (1 - \Pi)D_p] / 2b_f + \\ + \{ [a_f + (1 - \Pi)D_p]^2 / 4b_f^2 + (1 - \Pi)v_{imp}D_p / b_f \}^{1/2},$$

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

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

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

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 $k_0 = \frac{k}{b^{n+1}}$,

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

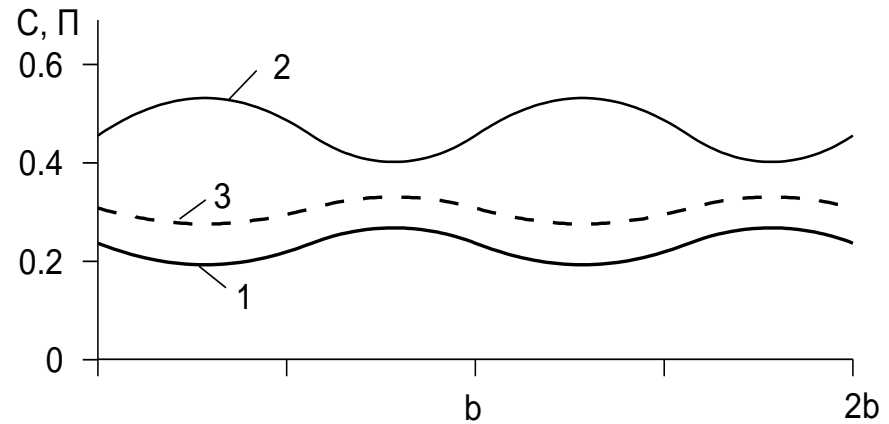
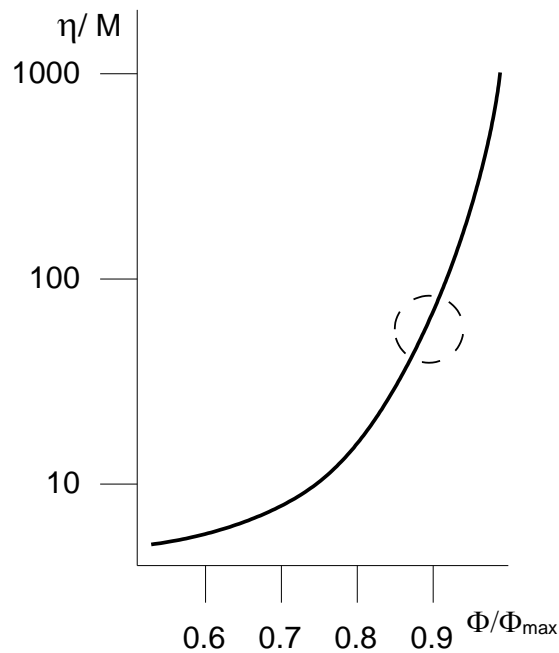
$$\left(\frac{D}{u} \frac{\dot{D}}{\dot{u}} \right) = 1, \quad \text{Mescheryakov's statistical criterion}^1$$

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

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

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.

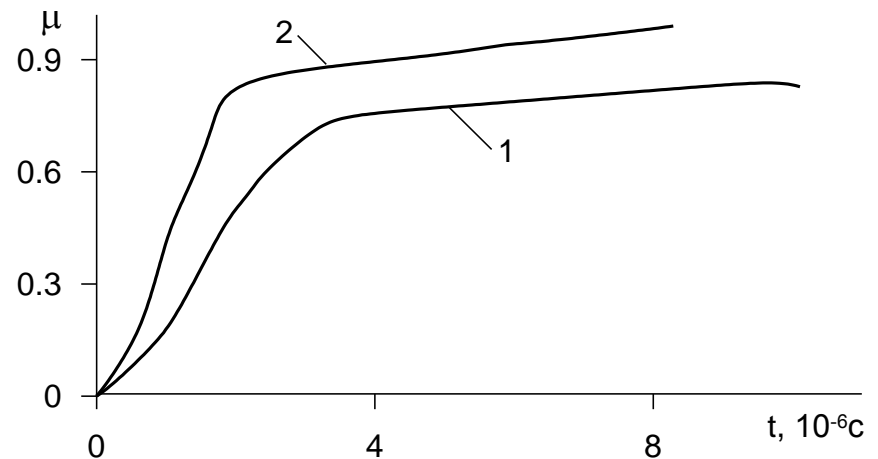
¹Mescheryakov Yu. I. // Control in Physicotechnical Systems, Fradkov, A.L., Ed., St. Petersburg: Nauka, 2004, pp. 222-245.



Curves: 1 - Ti; 2 - C; 3 - porosity

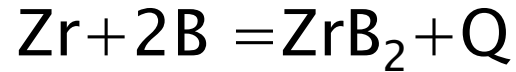
Dependence of mass fraction of reactive components on synthesis duration.

Shock pulse amplitude, GPa	5.6	14.5	24.0
Chemical reaction involved, mass %	- 0	+/- >50	+ 100

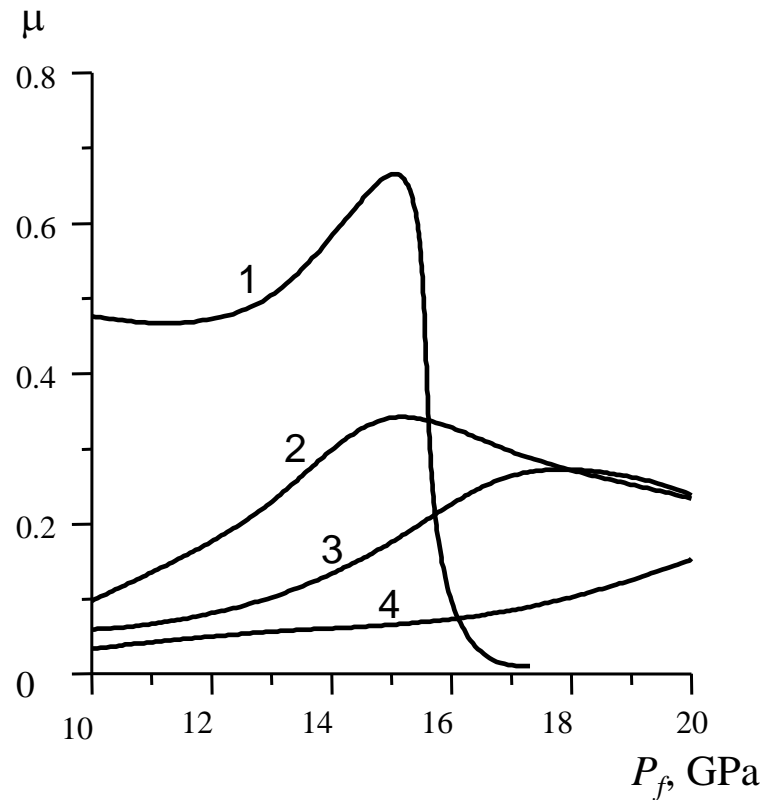
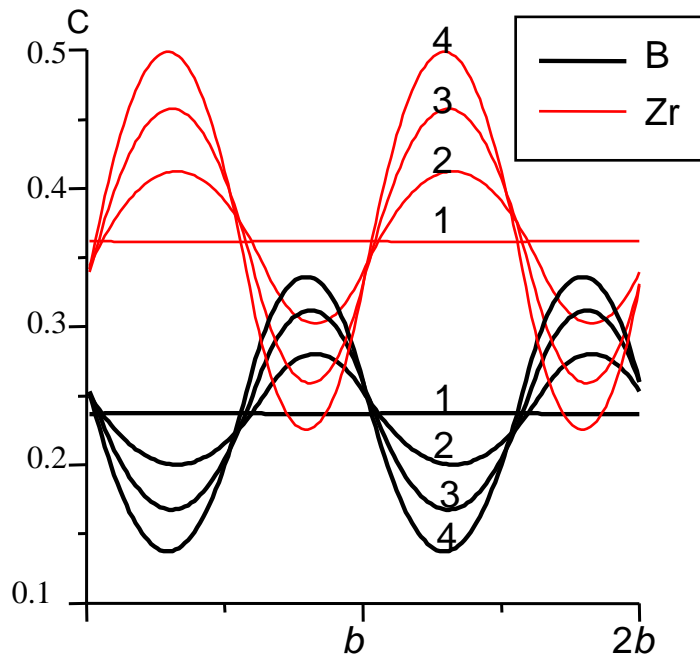


Curves: 1 - $Pf=14.5$ GPa; 2 - $Pf=24.0$ GPa. At $Pf=5.6$ GPa, necessary conditions for chemical transformation are not met

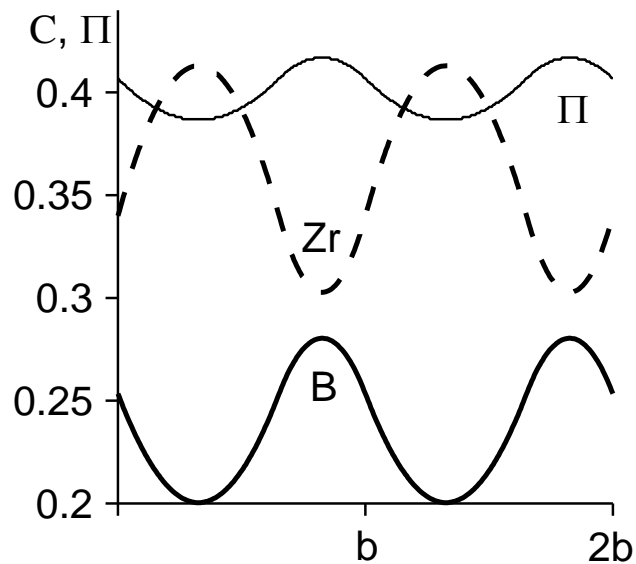
Computational experiments



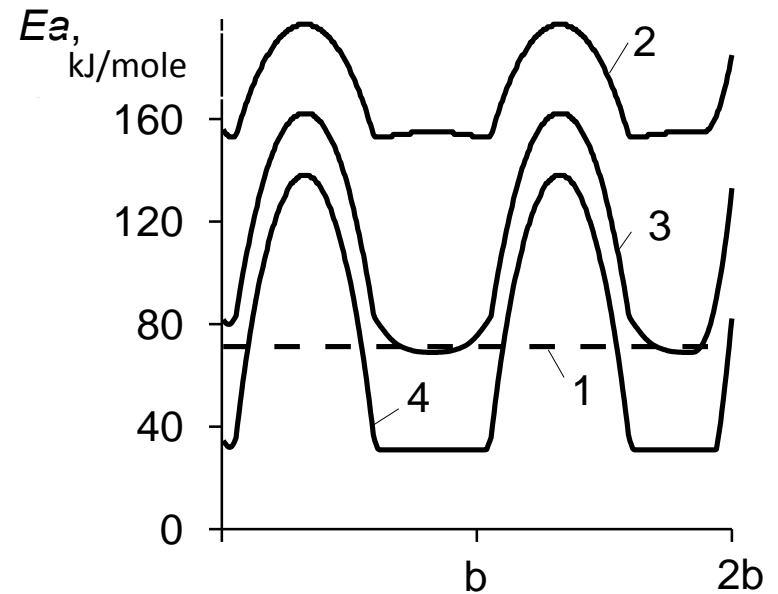
$d = 50 \mu\text{m}$, $P_0 = 0.4$, $T_0 = 293 \text{ K}$. $P_f = 3 \text{ GPa} \div 20 \text{ GPa}$.



The distribution of component concentration through the thickness of initial compact



The distribution of local values of activation energy



Curve 1 – critical values of activation energy; curve 2 – $P_f = 3$ GPa;
 curve 3 – $P_f = 5$ GPa; curve 4 – $P_f = 7$ GPa

Conclusion

The degree of mechanical activation of Zr–B mixture reactive components plays the key role in the satisfaction of the conditions of shock initiation of chemical transformations.

For the considered macroscopically heterogeneous powder mixture, shock initiation is possible in the areas with an excess of refractory component.

The change of internal friction mechanism is key feature of zirconium diboride shock synthesis.