

Computer Simulation of Dynamics of Reactive Systems

Vladimir N. Leitsin¹, Maria A. Dmitrieva^{1,2}, Tatiana V. Kolmakova²,

¹Immanuel Kant State University of Russia, Kaliningrad, 236000, Russia

² Tomsk State University, Tomsk, 634050, Russia.

1 Simulation conception

The powder mediums able to gasless exothermal chemical conversions are considered. Conditions of mechanochemical synthesis at dynamic (shock) loading of green compacts of reactive components mixture and inert filling agent are studied. The dynamic loading impulse can be generated at detonation of condensed explosive being in contact with initial compact or at collision of high-speed plunger with it. The matter compression is accompanied by collapse of pores and intensive mixing of the components, friction on the surface of particles and their deformation. In aggregate, these processes determine mechanical modification of powder materials [1].

In preparation of reacting compact a mixture of initial components undergoes premixing, activating, and pressing. Reacting powder mediums are characterized by presence of macroscopic structure of concentration heterogeneity formed in a process of powder compact preparation due to synergetic processes of discrete systems self-organization followed by formation of powder body's internal structure under intensive mechanical loading conditions. Formed at the stage of mixture preparation the structure of the mixture concentration heterogeneity can be modified in combustion wave and in a process of shock compression.

Real powder body is a modeling heterogeneous composition of reacting components A and B with inert filling agent having determined structure parameters, physical and chemical characteristics. Material of particles of one sort is considered to be homogeneous and isotropic with set physical properties. The structure of initial mixture is characterized by form and sizes of the particles and their units, their location, concentration of components and porosity. It is supposed that before shock compression the powders mixture of reacting components and inert filling agent has been preliminary pressed to state of close packing (compact) with defined values of medium porosity, characteristic dimensions of particles agglomerate and component concentration dispersion. At loadings a powder compact behaves as a porous body [1].

Macroscopic concentration heterogeneity of mixture is supposed to have regular spatial structure. Mixture with specified at an average concentration of components is inhomogeneous on volume of periodicity cell with size $a \times a \times b$ – reaction cell. Concentration heterogeneity of the element of macroscopic structure of mixture (cell) is set by changing the concentration of components in direction b in the assumption that required share of a low-melting component δ is concentrated at left side of the cell $a \times a$ in its part of size do to be defined by characteristic size of particles agglomerates (figure 1). For specified character of functions of distribution of mixture's volumetric concentration components (step-function or parabolic, for example) the parameter b/a can be used as the characteristic of

modeled macroscopic structure of mixture concentration heterogeneity. Side b of periodicity cell is chosen perpendicularly to the surface of mechanochemical conversions initialization. This direction is a principal direction of changing the reacting mixture structure in a process of mechanochemical conversions [2].

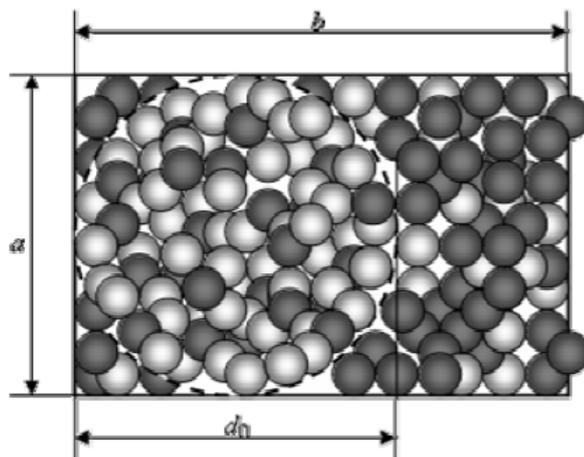


Figure 1. Concentration heterogeneity structure.

An element of macroscopic structure of concentration heterogeneity, reacting cell, is assumed to be representative volume of reacting powder medium considering structurally inhomogeneous powder material as a micro-inhomogeneous composite. In each section of a reactionary cell which is perpendicular to principal direction the statement about thermal homogeneity is accepted.

The mathematical model is a set of nonstationary problems of heat balance, of the shock modification of powder material, forced filtration, macrokinetics of chemical conversions, modelling of the modification conditions of the rear surface of powder compact at the exit of the shock pulse and modeling of the characteristics of heat and luminescent light of the side and rear surfaces of reacting powder compacts. Basic simulation conception [1] is supplemented with inhomogeneity of powders plastic deformation, phase transfer incubating time, gas phase formation possibility, powders damage level rheology during dynamic deformation, polydispersity of mixture taking into account. Thermomechanical and phase states of reactive medium are considered at macro and micro levels simultaneously. The possibility of transfer to non-equilibrium physical and chemical processes, resulting in nanostructure of synthesis product formation, initiation and realization of ultrafast chemical reactions at shock wave front is investigated.

The theoretical forecast of radiation temperature change of a sample surface of the reactive mixture, obtained by the technique [2], allows to separate thermal radiation from luminescent. In luminescent radiation differ chemiluminescence and mechanoluminescence. The combustion wave propagation in the sample is accompanied with the temperature gradient on its front that causes heat expansion and cracking of the powder mixture particles, which can be attended with the emission of light-mechanoluminescence.

General conception of simulation consists in follow:

1. Heterogeneous powder material, generated from the mixture of reactive components and inert filling agent, has a macroscopic structure of concentration inhomogeneity of components and porosity.
2. Mechanical activation is bound up with plastic deformation and destruction of surface layers of powder components particles. Compression of powder material results in thermal conductivity increase and structure inhomogeneity scale decrease, assisting the thermal activation of reactive mixture and synthesis intensity rise [1].
3. Local heating due to exothermicity of mechanochemical conversions can determine phase transfers and aggregative state change, including melting of low-melting component. At the melt zones powder medium is represented with solid skeleton saturated

with liquid phase. 4. An evaporation of a component is possible. 5. The porous mediums mechanics approach is applicable to simulation of mechanical behavior of powder body [2]. Shock compression is characterized by inhomogeneity of plastic deformation, so by inhomogeneity of mechanical activation by particles volume. 6. The law of conservation of energy of reacting powder layer is represented by a boundary problem with heat sources and sinks. 7. Filtration of melt of the low-melting component under porous pressure gradient provides convective heat and mass transfer. 8. Macrokinetics of chemical conversions is represented by multilevel model of reactive cell wherein the parameters depend on the structure scale, phase concentration, phase state, and on the degree of mechanical activation of reactive mixture [1]. 9. As a criterion of nanostructure of shock synthesis product formation is considered a fulfillment of conditions of non-equilibrium synthesis processes initiation at the initial stage of chemical conversions: achievement of necessary level of the mixture mechanical activation, change of reactive mixture aggregative state, fulfillment of statistical criterion of “turbulent” conditions of compression [3]. 10. An “initial” and a current level of reactive powders shock activation are considered. An instant part of damage level of reactive components particles at the shock impulse front and a damage level of material cumulated during incubating time [4] are determined. 11. Impulse (on intensity) processes of particles burning of a powder mixture cause chemiluminescent flashes. 12. The mechanoluminescence of the sample back surface can be caused by microspall fracture effects during the moments of a shock wave fronts exit and in the burning wave.

2 Results and Discussions

The conditions of the shock initiation of the chemical conversions are considered by the example of the powder mixture Ni – 31,5 mass. % Al. The model sample is characterized by the macroscopic structure of the concentration heterogeneity of the initial components $b/a=1,3$ (for homogeneous mixture $b/a=1,1$). The mixture of the reactive components with the particles size of $50\ \mu\text{m}$ which was previously pressed till the average value of the relative volume of pores $\Pi_0=0,4$ with the initial temperature of a layer $T_0=293\ \text{K}$ is considered. The shock loading of the layer of the powder mixture is modeled by the macroscopically plane shock pulse with the amplitudes $P_f=2\ \text{GPa}$.

Moments of fulfillment of nanostructure formation criterion in microlayers of model sample is represented in the figure 2a for initial model and for model with incubating time of damage.

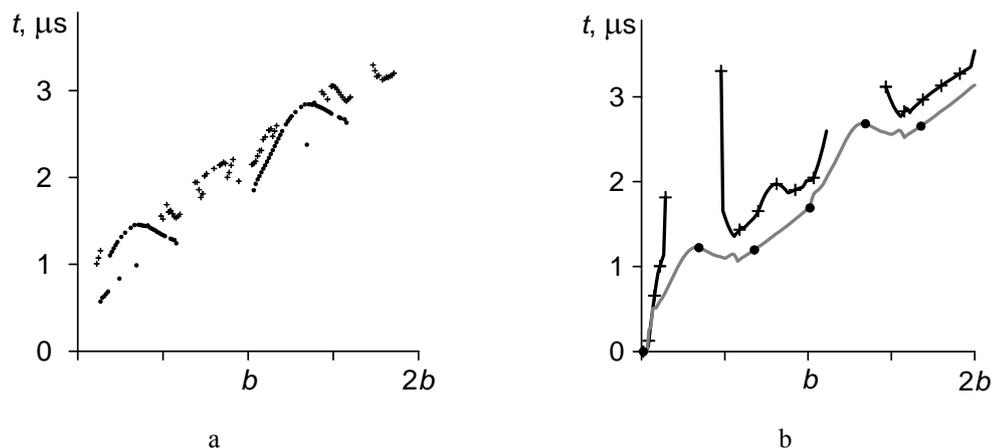


Figure 2. Moments of fulfillment of nonstationarity criterion (a) and moments of reaction initiation (b): • – initial model [1], + – specified model

As it follows from numerical experiments, introduction of damage incubating time parameter results in later moment of criterion fulfillment (relative to initial model), in turn it results in decrease of number of microlayers in which the nanostructure formation is possible. In the figure 2b moments of reaction initiation are represented for reactive layer consisting from 2 reactionary cells. Specification of the

model of mechanical activation of powder materials result in significant difference of results of shock synthesis condition. Inhomogeneous character of chemical conversions initiation is observed, so an impulse character of combustion processes is predicted. Nanostructure formation is possible solely at the microlayers where the reaction initiation took place.

Research of the rear surface radiation parameters was carried out for the model sample NiO+Al+25%Al₂O₃. The shock loading of the powder mixture is modeled by the shock pulse with the amplitudes $P_f=2$ GPa (figure 11a) and $P_f=8$ GPa (figure 11b). The character of chemiluminescence is similar for the investigated pressures of the shock wave. The maximum chemiluminescence flashes correspond to the temperature increase of the heat radiation accompanied with the step change of the intensity of chemical conversions. The first chemiluminescence flashes are observed at the first moments; it proves the initiation of the chemical conversions directly after the shock wave front in the most mechanically activated subareas of the rear surface. The flashes in the future periods are caused by the heat ignition of the low activated subareas. The time reduction between the bursts as well as the reduction of the total chemiluminescence for $P_f=8$ GPa in comparison with the results for $P_f=2$ GPa reflect the difference between the degrees of the mechanical activation of the reactive components.

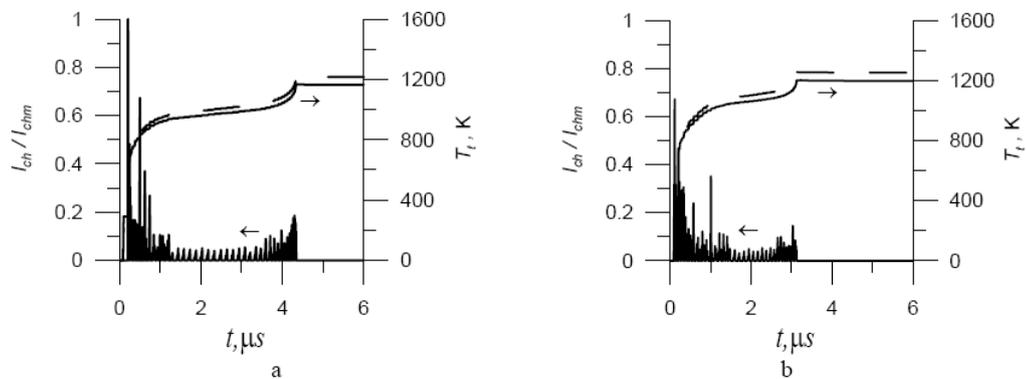


Figure 11. The distribution of the heat radiation temperature T_t on two wave-length ((- -) – 420 nanometers, (—) – 720 nanometers) and relative intensity of chemiluminescence I_{ch}/I_{chm} of the rear surface of the model sample.

In summary, the following conclusions can be drawn: For ultradispersed powder reactive materials zones of nonstationary condition of dynamic compression are most probable regions of nanostructure formation. Considering the incubating times of powder components modification allows to apply the model for shock synthesis of nanocomposites. The characteristics of thermal and luminescent emission from the surface of reactive powder compacts account for the parameters of state of the reactive medium, attainable pressure levels, and kinetics of the relevant chemical reactions. That means that the obtained results can serve as a basis for development of contactless methods for monitoring the physicochemical processes in reactive powder materials.

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