A Model of the Synthesis Processes in Reacting Powder Compacts of Ti–Al, Ti–C Types under Shock Loading

V. N. LEITSIN and M. A. DMITRIEVA

Tomsk State University,
Pr. Lenina 36, Tomsk 634050 (Russia)

E-mail: leitsin@ftf.tsu.ru

Abstract

The mechanisms of synthesis processes and mechanochemical reactions in the dynamically loaded layer of a powder mixture able to undergo gas-free self-propagating high-temperature synthesis (SHS) are investigated by means of computer simulation. Within the model of reacting powder medium, the related problems of shock compaction, establishment of thermal balance, filtration of a melt of the low-melting component, and macrokinetics of chemical transformations are considered. We take into account the macroscopic structure of concentration non-uniformity of the initial powder mixture, the possibility of mechanical activation of the reacting components during shock compression, and modification of the parameters of state and structure at all the stages of synthesis. The plastic deformation of crystal structure and destruction of the surface layers of powder particles are considered to be the decisive factors of mechanical activation. The model of reaction cell of Arrhenius type with variable macrokinetic parameters is used. The activation energy of the reacting mixture is considered to be a linear function of the work of plastic deformation and the work of destruction of the surface layers of particles. The pre-exponential factor agrees with the power-behaved reaction diffusion. The powder body is represented by a model system of powder components with the given structural parameters, physical and chemical characteristics; the structure of the powder layer is represented by the model regular structure of the cells of concentration non-uniformity. Powder mixtures of Ti–Al and Ti–C types preliminarily pressed to the required mean porosity are considered in the computational experiment. The factors determining changes in the reactivity of the reacting powder mixture during mechanical load are considered, as well the effect of the formation of a structure with nanometer-scale morphological elements are investigated.

INTRODUCTION

Reacting powder media prone to gas-free exothermal chemical transformations are considered [1]. Intense mechanical action on the reacting components or mixtures causes an increase in the reactivity (mechanical activation) due to the plastic deformation of the crystal structure and removal of the oxide and adsorbed layers from the particle surface of the powder mixture [2, 3]. The solid-phase regime which is possible after mechanical activation allows one to conserve the structure of the material prescribed at the stage of the formation of an initial powder compact, dynamic compaction of the reacting powder mixtures provides consolidation and proper conditions for chemical transformations to occur; evident technological advantages are thus provided.

Modern mechanics of the reacting powder media under deformation develops at the junctions between mathematical modelling, mechanics of powder materials, mechanics of reacting media, theory of heat and mass exchange, combustion and chemical kinetics. Modelling is based on the following concept of the description of physicochemical processes in reacting powder media [4]:

1. Heterogeneous powder material formed from a mixture of reacting components and an inert filler possesses a macroscopic structure of non-uniformities of the component concentrations and specific pore volume.

2. Mechanical action of a powdered mixture of reacting components can cause an increase in the reactivity of the mixture.

3. It is possible to compact the powder material of Ti–C type in which a high-melting

framework possesses low resistivity to shift load; compaction is accompanied by a change in the mechanism of internal friction of the powder medium due to melting of the surface layer of one of the reacting components as early as at the very first stages of straining.

4. Preliminary pressing of the powder mixture ensures the formation of bonds between particles; that is why the approach provided by mechanics of a solid body under deformation is applicable to the modelling of the mechanical behaviour of a powdered body.

5. Heating caused by exothermal character of chemical transformations can determine phase transitions and melting. In the latter case, the reacting powder medium acts as a solid-phase framework saturated with the melt of a low-melting component.

6. A melt of the low-melting component of the powder mixture can move in the porous solid-phase framework under the action of pore pressure providing convective heat and mass transfer.

7. The macrokinetics of gas-free exothermal transformations is represented as a multilevel model of the reaction cell of Arrhenius type. Possible centres of transformations are considered to be spread over the volume of the reaction cell proportionally to the stoichiometric fraction of the reacting components and to be initiated at the moment when the critical reactivity parameter is achieved.

A real powder body is a model heterogeneous mixture of the reacting components with an inert filler; the mixture possesses determined structural parameters, physical and chemical characteristics. The physico-mechanical properties of the component particles are considered to the represented by the corresponding material functions known for bulk samples (depending on temperature, porosity, *etc.*). The initial structure of a powder body is characterized by the size of particles and their aggregates, their arrangement, concentration of components and porosity.

The behaviour of a layer of the powder material loaded in the cross direction by a macroscopically flat pulse of the given amplitude and duration is investigated. At each moment of time, the characteristics of mechanochemical processes, effective parameters of the state of medium, concentration and phase characteristics of the structure are considered to be constant over the sections of the reacting powder body perpendicular to the direction of loading. Such an approach allows us to formulate the problems of modelling physicochemical processes in one main direction: to the depth of the powder layer.

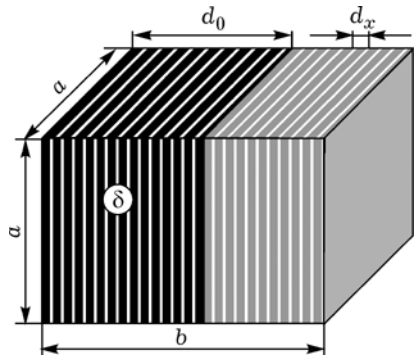

Fig. 1. Cell of the concentration non-uniformity. For designations, see text.

The reacting layer is modeled by a sequence of reaction cells with the microlayer thickness d_x; each of the cells is an element of the macroscopic structure of concentration non-uniformity of the reacting powder mixture (Fig. 1). The mixture with the given mean concentration of components is non-uniform over the volume of the periodic cell with dimensions $a \times a \times b$. The concentration non-uniformity is governed by changes in the concentrations of components along direction b, assuming that the given fraction of the low-melting component δ is concentrated at the left-hand face of the cell $a \times a$ in a part with a size d_0 determined by the characteristic size of particle agglomerates. For a given character of the distribution functions for the volume concentrations of mixture components (for example, stepwise or parabolic spline), the b/a parameter can serve as a characteristic of the modeled macroscopic structure of concentration non-uniformity.

A scheme of mathematical modelling taking into account the connection between the kinetics of chemical transformations and the processes of mechanical modification of the powder compact under mechanical consolidation, phase transitions of the components, establishment of thermal balance, convective mass transfer is built. It is proposed to use the

known parameters of the final state of the porous medium behind the front of macroscopically flat shock pulse as the mean macroscopic parameters [5]. At the microscopic level, the mechanical behaviour of the powder medium is investigated within the model of Nesterenko unit cell [6] which is applied at each step in time and per each component [7].

The energy method is used to estimate the processes of dynamic modification. Thermodynamics of the shock compression of a powder body is described by the relations for mean dissipated energy for the plastic and viscous flow of components, energy of movement under pore collapse, work of destruction of the surface layers of powder particles. The difference between specific power of compression and specific energy dissipated for plastic deformation is microkinetic energy which is consumed for purification of the surface contact layers of particles, for their dispersion and possibly for viscous compaction of the powder material. It is considered that each moment of the action of mechanical load pulse affects the powder medium with the current porosity, temperature, concentration and phase characteristics, and other parameters of state. The possibility to realize different mechanisms of compaction is estimated on the basis of the achievement of threshold values of plastic deformation of the components, pressure of the shock pulse, and the internal energy of the powder mixture under deformation absorbed at the loading step [7].

The work of destruction of the surface layers of particles provides activation of the reacting components of powder mixture; in addition to the work of plastic deformation of particles, it determines the sources of heat in the equations of thermal balance.

The problem of thermal balance allows us to estimate the enthalpy of the framework of powder medium and filtering liquid phase in all the sections of the powder layer taking into account phase transitions in the material of components, thermal conductivity, the presence of heat sources of chemical and mechanical nature, convective heat exchange between the framework and the flow of liquid phase, thermal conductivity of the immobile liquid phase [8].

When modelling the convective mass transfer of the liquid-phase component, one may neglect capillary forces, Archimedes forces, capillary osmosis, *etc*. It is proposed to consider the forced filtration of the liquid phase under the action of thermo-capillary forces and pore pressure during the action of mechanical load pulse, taking into account the bearing strength of the solid-phase framework, which is determined by the dependence of effective yield stress on temperature. In the saturated porous medium, one may neglect viscous strain in the liquid phase, forces of inertia, pulsation transfer of pulse and the kinetic energy of pulse motion. Therefore, a connection between the rate of liquid phase filtration and the pressure gradient in the saturated porous isotropic medium follows from the pulse conservation law, in agreement with the linear Darcy law [9]. The problem of filtration of the melt of low-melting component is considered for two adjacent microlayers of the powder body.

The macrokinetic equation fro the rate of chemical transformations $\partial z/\partial t$ is represented as a product of the Arrhenius function of temperature and the braking function $\varphi(z)$ of the degree of transformation, which is determined by the type of reaction [10]

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

In the model of the reaction cell, the preexponential factor k_0 is considered to be structurally dependent; it is determined for the whole representative volume taking into account its deformation; the activation energy parameter E_a is considered to be local and is determined at the microscale by the energization of initial components in the microvolumes of the mixture. The behaviour of the macrokinetic braking function is determined at the microlevel by the type of reaction at each moment of time depending on the phase and concentration states of the microlayer. The possibility for reactions to proceed according to the types of solid-phase transformations of components and in the presence of the liquid phase is taken into account.

Keeping in mind that the thickness of the formed layer of reaction product meets the power law of reaction diffusion, we consider the preexponential factor to be dependent on the size of the structural element of concen-

tration non-uniformity [4]: $k_0 = k/b^n$, where k is the k_0 value for the reaction cell of unit thickness, n is the order of the power law [11].

Changes in the reactivity of the powder mixture under mechanical action are taken into account by assigning the parameter of activation energy of chemical transformations as a linear function of the work fulfilled during mechanical activation [4]:

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

Here E_0 is activation energy in the absence of mechanical action; H is Heavyside function; P_i^* are the critical values of shock pulse P determining involvement of one or another mechanism of activation; α_i are parameter determining the contribution from the work of mechanical action A_i which changes the reactivity of the mixture according to mechanism i.

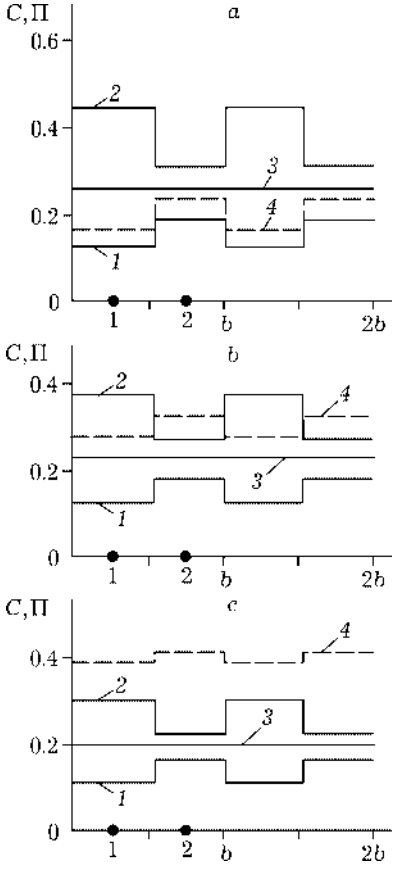

Fig. 2. Distribution of initial concentrations of components in Ti + Al + 33.3 % $TiAl_3$ mixture and the specific pore volume over the thickness of the layer composed of two reaction cells for different initial porosity Π_0 (b/a = 1.5): 0.2 (*a*), 0.3 (*b*), 0.4 (*c*); *1* – Ti, *2* – Al, *3* – $TiAl_3$, *4* – П; points in which modification of the reaction cell parameters during mechanical load is observed are marked at the abscissa axis.

The α_i and k coefficients are the matching parameters of the reaction cell model of the reacting powder material; these parameters are determined when modelling the laboratory experiments.

The condition of reaction equivalence of the states of reacting mixture differing in activation energy at the moment when chemical transformations are launched can be considered as the equality of reactivity parameters [4]:

$$\beta = \frac{E_a}{RT} = \frac{E_0}{RT_0} = B$$

Here T_0 is the experimentally determined temperature at which chemical reactions are launched; it corresponds to the activation energy E_0.

The solutions of all the problems considered herein are bound through the iterative refinement of all the model parameters at each moment of time.

The factors determining changes in the reactivity of the reacting powder medium during mechanical loading are investigated. Investigation is carried out for the model Ti–Al powder system with inert $TiAl_3$ filler. A stepwise distribution function for the concentrations of the components of model powder mixture is considered (Fig. 2).

The results of prediction of the relative parameter of reactivity β/B depending on porosity and temperature of the initial powder compact, amplitude of shock pulse and the parameter of concentration non-uniformity in the microlayers of the cell corresponding to observation sites *1* (continuous curves) and *2* (dashed curves) are shown in Fig. 3. The $\beta/B = 1$ value corresponds to the criterion of the launch of chemical transformations.

The results obtained in the investigation allow us to make the following conclusions:

1. The degree of mechanical activation is a local characteristic of the micro-volumes of the reaction cell.

2. A possible degree of mechanical activation decreases with an increase in the temperature of the powder mixture.

3. With an increase in the initial porosity of the reacting powder medium, the possible degree of mechanical activation increases up to a definite limiting value.

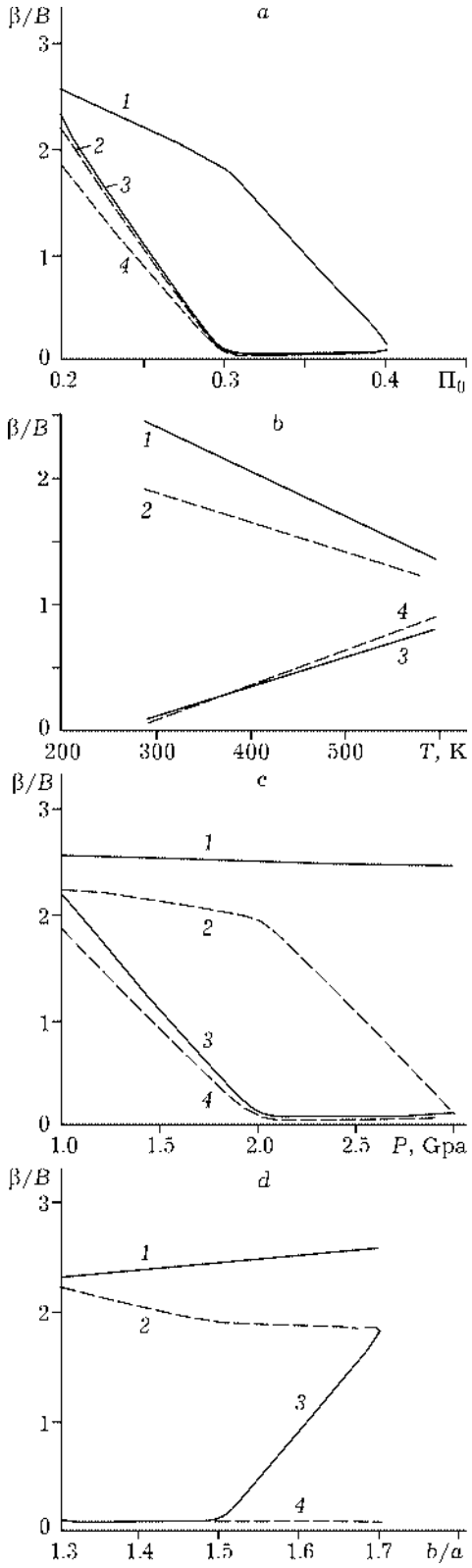

Fig. 3. Dependenceis of the relative parameter of reactivity on the parameters of the model of reacting powder medium: *a* – P = 2 GPa, T = 293 K, b/a: 1.3 (*1*, *2*), 1.7 (*3*, *4*); *b* – b/a = 1.5, P = 2 GPa, Π_0: 0.2 (*1*, *2*), 0.4 (*3*, *4*); *c* – b/a = 1.5, T = 293 K, Π_0: 0.2 (*1*, *2*), 0.4 (*3*, *4*); *d* – P = 2 GPa, T = 293 K, Π_0: 0.2 (*1*, *2*), 0.4 (*3*, 4).

4. The parameters of the structure of concentration non-uniformity (the dimensions of structure element, the degree of non-uniformity of component concentration and specific pore volume) are the determining factors of an increase in the reactivity of the reacting powder mixture together with the amplitude of the dynamic action.

Materials with the size of morphological elements below 100 nm in at least one direction possess unusual atomic crystal lattice and exhibit unique properties [12]. The small size of crystallites which are the morphological elements of nanocrystalline materials determines high level of strain and defects. A decrease in grain size down to the nanometer scale causes an increase in hardness and yield stress by a factor of 4–5 within temperature range from 10 K to Debye temperature. Thermal capacity of nanopowders within this temperature range is 1.2–2 times as large as thermal capacity of bulk materials [13].

Let us consider that after the achievement of the limiting degree of plastic deformation of the ultrafine reacting component of the powder mixture in the microlayer of the reaction cell, the size of particles along one direction becomes less than 100 nm, and the formed particles of the product of chemical transformation are of the similar size. Since this moment, we use the parameters characteristic of the nano-structural state as the material functions and constants.

The results of computational experiment are shown in Fig. 4. A sample of the powder mixture Ni + Al + 33 % NiAl with the initial temperature T_0 = 293 K and particle size d = 4.5 μm pressed preliminarily till the specific pore volume Π_0 = 0.3 is considered. In all the plots, curves *1* correspond to the results of experiment taking into account the possibility to form a structure with nanometer-sized morphological elements; the results represented by curves *2* were obtained without taking into account the formation of nanostructures.

Among the effects of the formation of the structure with nanometer-sized morphological elements, we should note: 1) the possibility to achieve the high degree of mechanical activation; 2) a change of the regime of mechanochemical transformations; 3) an increase in

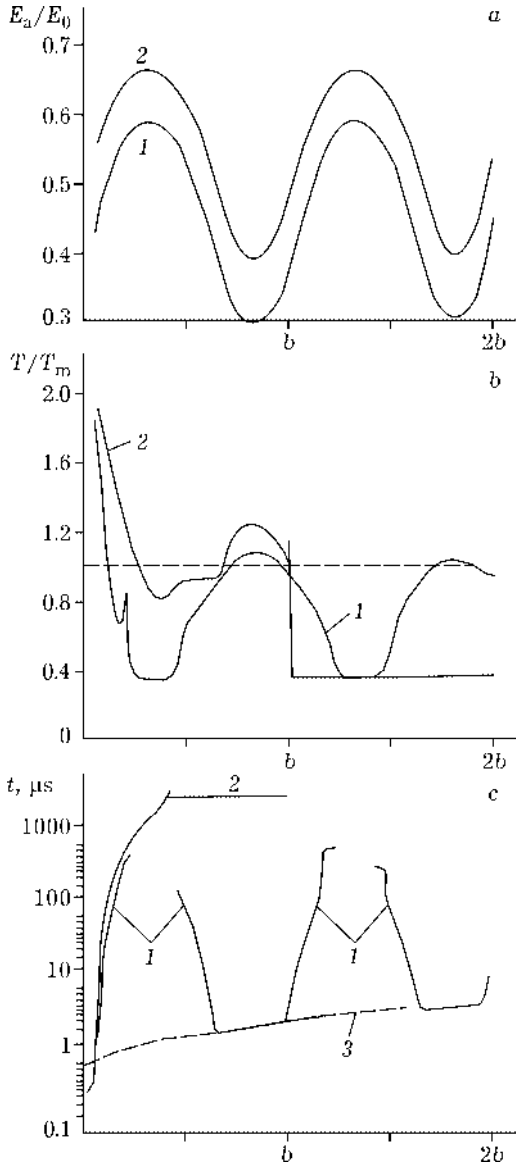

Fig. 4. Results of computational experiment on estimation of the effects of the formation of a structure with nanometer-sized morphological elements. For designations, see text.

the intensity of chemical transformations; 4) a decrease in the temperature of shock synthesis.

CONCLUSIONS

The morphology of agglomerates of the reacting mixture obtained in mechanical devices and described in [14], and the achieved degree of mechanical activation are similar to the structure and reactivity of the reacting powder layer modified during the shock load. The products of mechanical activation in a planetary mill change their morphology. During the multi-cycle mechanical treatment in a planetary mill, the powder particles of the initial reagents form dense layered composite agglomerates undergoing substantial plastic deformation and dispersing. This fact allows us to explain anomalously low temperature and high rates of the solid-phase combustion of the reacting powder systems Ni-Al, Ni-Ti, Ni-Si and a number of others after mechanical activation of the reaction mixtures in a high-energy planetary mill [14].

Acknowledgements

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