The study of microstructure and propagation of the combustion wave of SHS in nanodimensional multilayer systems of Ni-Al with using molecular-dynamic simulation

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Abstract. Computational experiments (CEs) on the molecular-dynamic simulation of the propagation of the combustion wave of the SH-synthesis process in a stack of alternating layers of nanoscale crystal lattices of Ni and Al atoms have been carried out. In the calculations are used two versions of the interatomic interaction potential in the "embedded atom model" (EAM) and the LAMMPS package taking into account parallel computings. As the results of computational experiments for two varieties of the EAM potential, a family of temperature profiles along the layers of the structure at successive instants of time (up to 40 ns) and the corresponding set of microsections (snapshots) of the layered structure are given. For large values of the initial heating temperature and the stoichiometric ratio of Ni and Al atoms in the SHS sample, the computational experiments were confirmed the heterogeneous SHS-reaction mechanism, referred to in scientific publications as "mosaic-dissolution-precipitation". In addition, when under such conditions a combustion wave of SHS passes through, the effect of heat localization is observed with the establishment of a higher temperature in the final region of the sample compared with the initial region, as a result of which on the "plateau" of the temperature profile corresponding to 16 ns a smooth "dip" is observed. Then, at subsequent times, there is a continuation of combustion (more precisely, after combustion) in the inverse direction with the equalization of the temperature plateau corresponding to a higher temperature value of the final region of the SHS-sample.

1. Introduction

The method of "self-propagating high-temperature synthesis (SHS)" is used as one of the effective methods for obtaining modern functional materials with specified properties. In the process of SH-synthesis, under the action of a heat pulse in a thin layer of interacting reagents of the pressed sample occurs an exothermic combustion reaction, which spontaneously propagates through the sample by heat transfer from layer to layer. The diversity of micro-, meso-, and macrostructures of SHS products largely depends on the initial structure of the particle packing of the reacting mixture and other reaction parameters (the dispersity of the reagents, their initial ratio, initial temperature and porosity of the mixture, degree of dilution, heat losses and other factors). The stability of the motion of the combustion wave front is affected by the heterogeneous distribution of the initial reagents in the structure of the powder mixture, and therefore the temperature, velocity and direction of propagation of the combustion wave change quasiperiodically. The so-called "SHS discreteness" problem is determined by the presence of "microfires" of combustion in the wave structure, so the actual task is to analyze the microheterogeneous structure of the combustion wave, which is most often solved by experimental methods. To study the evolution of the discrete decay of the thermal structure of the SHS wave and the combustion kinetics in locally unstable modes of microheterogeneous combustion, it is necessary to refine the physicochemical and mathematical model concepts, which plays an important
role in optimizing the technological modes for the SH-synthesis of materials with specified functional and operational properties.

Some model concepts of the microheterogeneous combustion mode in the SH-synthesis of nickel aluminides in model "layered" structures of the Ni-Al binary atomic system (figure 1) are considered.

A study of the microheterogeneous combustion regime in model "layered" structures of the Ni-Al system was carried out using the molecular-dynamics simulation (MDS) method in the LAMMPS software package using its ability to apply parallel computations [1].

The possibility of studying the regime of microheterogeneous combustion and on this basis during the SHS process of recognizing the local instability of motion of the combustion wave makes it possible to timely control of the SHS process to ensure its stability and homogeneity throughout the bulk of the powder mixture. This aspect of the problem is relevant and important in the practical application of SHS for the production of finished products of metal and cerments in the field of additive technologies. The temperature and propagation velocity of the SHS combustion wave through the molded powder mixture of the initial reagents are the main controlled technological parameters.

2. Stages of molecular-dynamic simulation of SH-synthesis of nickel aluminide in the LAMMPS package using parallel computations

In the MDS method, a discrete-continuum simulation approach is implemented. Namely, as a basis for describing the time evolution of the system, Newtonian mechanics is used, and the system itself is represented as an ensemble of particles (as material points). The evolution of the system is modeled by integrating the equations of motion of individual particles on the basis of a simple potential interaction with a constant time step. Simulation the evolution of a system of "large" particles (individual granules of a material) by the MDS method gives its macroscopic description. Simulation of atomic clusters and nanosystems is performed at the atomic level: quantum effects are encapsulated in the function of the potential to refine the features of the interaction of the system atoms. Even taking into account the deterministic nature of Newtonian mechanics, adding chaotic thermodynamic motion to the model with, for example, specifying random initial velocities in accordance with Maxwell's distribution allows us to approximate simulation results to the real behavior of the system and obtain data on the macroscopic characteristics of the object. The MDS method is widely used in the field of biochemistry, but the advantages of the method can be used to accurately determine the microscopic structures of materials, to simulate nanoobjects in order to study their properties and to find methods of synthesis.

Using the MDS method in the LAMMPS package supporting parallel computations, the propagation of the combustion wave in the SH-synthesis of nickel aluminide was simulated.

Each "large" layer of the structure in the original layered structure of the Ni-Al mixture (figure 1) consists of several atomic layers (atomic planes) forming a crystal structure (lattice) of elementary crystalline cells of the fcc type with the parameters: for Ni, the parameter $a = 0.3524$ nm, $a = 0.405$ nm for Al [2, 3]. The ratio of the number of atoms is $N_{Ni} / N_{Al} = 3.94$, i.e. the fraction of Ni atoms is equal to $n = 0.7975$ (79.75%).
The initial temperature of the sample (figure 1) is assumed to be 600 K, and at this temperature, the entire structure was "relaxed" for 0.4 ns with fixed thermodynamic parameters: the number of atoms $N = 717410$, the external pressure $P = 1$ Bar, and the temperature $T = 600$ K (NPT-ensemble). At this stage of the simulation, periodic boundary conditions were established for all 3 dimensions. Periodic boundary conditions are preserved for the entire sample and in the next stage. Within 0.1 ns at this stage, the structure is heated from 600 to 1200 K in the initial region of the sample (50x1.4x15 nm) under the conditions of the NVT ensemble, where V is the volume of the heating region. For the system of atoms in the remaining region of the SHS sample with dimensions (370x1.4x15 nm) during this same time period, the conditions of the NVE ensemble (E-total energy of the atoms) are established. Then begins simulation of the propagation of the SH-synthesis wave with the preservation of the conditions of the NVE ensemble for the whole SHS-sample. On the boundaries of the calculated region along the X axis, then "free" boundary conditions are imposed, and periodic boundary conditions remain along the Y and Z axes.

In the computational experiments (CEs) for the Ni-Al system evolution simulation were used two varieties of the interatomic interaction potential in the "embedded atom model (EAM)"; EAM-potential of the 2002-th year [2] and EAM-potential of the 2009-th year [3].

By means of the boundaries of the "plateau" of each temperature profile (figure 2) for the EAM-potential of the 2002-th year (designated EAM_2002) was estimated the velocity of the combustion wave front, approximately equal to 35 m/s, i.e. the combustion kinetics for micro- and nanosized samples of layered structures (nanofoils) develops two orders of magnitude faster than in macrosized samples.

![Figure 2](image)

**Figure 2.** Set of temperature profiles as functional dependencies of the combustion temperature of SHS vs. the coordinate X for consecutive moments of time (potential EAM_2002, the external pressure $P = 1$ Bar).

The combustion wave reaches the end of the sample (coordinate 420 nm) in about 12 ns. In paper [4], analogous conditions for carrying out the CEs and analogous scheme of the layered structure are given. However, the warm-up time of the initial zone in [4] was 0.08 ns, i.e. to 0.02 ns (or 25%) less than the 0.1 ns time set in the CE by the authors of this paper. In [4], the velocity of the combustion
wave front is given, equal to 20.13 m/s, which is noticeably less than 35 m/s (figure 2). Most likely, the difference in the values of the velocity of the front motion can be explained by the longer warm-up time of the initial zone of the sample set in the CEs by the authors of this paper. The temperature corresponding to the "combustion plateau" of the time of 18 ns in [4] is 1260 K, which is fairly close to the corresponding value of the temperature "plateau" (approximately 1250 K), which is reflected in figure 2.

When using the EAM-potential of the 2009-th year (designated EAM_2009), the estimate of the velocity of the combustion wavefront (figure 3) is approximately 25 m/s, and the combustion wave reaches the end of the sample slightly less than 16 ns.

![Figure 3: Set of temperature profiles as functional dependencies of the combustion temperature of SHS vs. the coordinate X for consecutive moments of time (potential EAM_2009, the external pressure P = 1 Bar).](image)

In [5] analogous conditions for the simulation of CEs are given, as in [4], with the same time of 0.08 ns for heating the initial zone of the sample from 600 to 1200 K, but these conditions are given for the potential EAM_2009. For an initial relaxation temperature of 600 K (figure 4.a, [5]) and for the value of the fraction of Ni atoms that coincide with the value $n = 0.7975$ of this paper, the estimate of the velocity of the combustion wave in [5] is approximately equal to 20 m/s. This value was also less than the value 25 m/s received by the authors of this paper, which can also probably be explained by the more long warm-up time (0.1 ns) of the initial zone of the sample of the authors of this paper. Analyzing figure 3, we can say that the combustion wave reaches the end of the sample (coordinate 420 nm) in about 16 ns (the temperature plateau has a "dip" in the middle part of the SHS-sample), and the corresponding temperature of the final region is estimated in the range 1560-1570 K (the combustion temperature of the initial region of the sample is lower, i.e. in the range 1500-1510 K). In subsequent times (from 16 to 40 ns), the temperature of the final region becomes even higher (about 1670 K), and the dip on the temperature plateau "disappears". In [5] there is no data for the
corresponding graphical dependence for the fraction of Ni atoms equal to \( n = 0.7975 \) for the relaxation temperature of 600 K (figure 4.b, [5]). Extrapolation of this dependence to the point \( n = 0.7975 \) gives an estimate of the combustion temperature above 1400 K.

Computational experiments in which the external pressure instead of 1 Bar was set equal to 0\( (P = 0 \text{ Bar}) \) with all the remaining parameters retained the same, practically repeated all the results. To confirm this fact, the corresponding figure 4 is given below.

![Figure 4](image)

**Figure 4.** Set of temperature profiles as functional dependencies of the combustion temperature of SHS vs. the coordinate \( X \) for consecutive moments of time (potential EAM_2009, the external pressure \( P = 0 \text{ Bar} \)).

Using the software package OVITO [6], designed to recognize and visualize the structures of elementary cells in simulated atomic and molecular systems, an analysis was carried out of the allocation structures of Ni and Al atoms in the structure of the SHS-sample at consecutive times of SH-synthesis (figures 5 and 6 for the two varieties of the EAM potential).

At successive instants when using the EAM_2002 potential in the CEs, figure 5 shows the allocation structures of Ni and Al atoms, which qualitatively correspond to the similar structures presented in [4], and which confirm the difference in the velocity values of the combustion wave obtained in [4] and in the CEs of authors of this article. The evolution of the structure (figure 5) corresponds to the reaction mechanism "of dissolution and crystallization from the melt".

With the use of the EAM_2009 potential the results of the CEs, reflected in figure 6, confirm the dynamics of the evolution of the mosaic pattern along the sample at successive instants of time, as in the article [5], which refers to the experimental confirmation of mosaic structures in the form of transmission electron microscopy images (TEM). The mosaic structure is formed as a result of a change in the regime of "dissolution and intermetallic phase crystallization from the melt" to the regime "dissolution with precipitation of intermetallic phase in the form of a solid phase" regime. In [5] the following conditions for mosaic manifestation are substantiated: \( n > 0.5 \) and the relaxation
temperature should be greater than 400 K (in our case, $n = 0.7975$ and the relaxation temperature is 600 K).

Therefore, the simulation results of the process of combustion wave propagation using the EAM_2009 potential is a correct result compared to the results obtained using the potential EAM_2002.

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**Figure 5.** Set of the microsections (snapshots) of the distribution structure of Ni atoms ("khaki" color dots) and Al atoms (dark blue dots) along the sample at successive instants of time: the intermetallic phase corresponds to the "gray" dots in the homogeneous zone (on the left) at the beginning of the sample and in two diffused layer (potential EAM_2002).

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**Figure 6.** Set of the microsections (snapshots) of the distribution structure of Ni atoms ("khaki" color dots) and Al atoms (dark blue dots in the mosaic layers from 2 to 14 ns inclusive) along the sample at successive instants of time: the intermetallic phase corresponds to the "gray" dots in the homogeneous zone (on the left) at the beginning of the sample and in the diffused mosaic layers from 16 to 40 ns (potential EAM_2009).

Analyzing figure 3, when the combustion wave of SHS passes, for example, left-to-right, the effect of heat localization is observed with the establishment of a higher temperature in the final region of the sample compared with the initial region, resulting on the "plateau" of the temperature profile of 16 ns there is a smooth "dip". Then, in subsequent times (from 16 to 40 ns), the continuation of combustion (or, to be more exact, aftercombustion) in the right-to-left direction is observed, with the temperature plateau aligned with the temperature of the final region of the SHS-sample (at a higher temperature value of 1670 K). Since the temperature in the final region of the SHS-sample becomes 1670 K (approximately 1400 °C) at the time of 40 ns, and the fraction of Ni atoms is $n = 0.7975$ (79.75%), according to the phase-equilibrium diagram of the Ni-Al system, in the SHS-sample can occurs processes of formation and decomposition of intermetallic phases. With a high degree of probability, "multiple" SHS process (MSHS) can occur, which is observed only in bilayer films. The reaction products "multiple" SHS process are eutectic phases [7]. MSHS is a new reversible autowave
eutectic phase transition [7] and consists in the fact that a very large number of times can be initiated on the same SHS-sample.

The above-mentioned passage of the combustion wave to the final region of the SHS sample to 16 ns is confirmed by the microsections of the mosaic structure (figure 6). Namely, the initial two horizontal layers with liquid Al, displayed in blue in figure 6, at that point in time lose the clarity of the blue color, since the layers of liquid Al in accordance with the mechanism of "mosaic of reactive dissolution-precipitation" are "filled" with a solid intermetallic phase NiAl, starting from the boundaries inside these layers [5]. In the time interval from 16 to 40 ns, the process of aftercombustion takes place in the inverse direction at a higher temperature of 1670 K, which is also confirmed on figure 6 by the increase in the blurriness of the blue color with time (the movement of the boundary of blurriness of the blue color with time proceeds right-to-left).

Using the software package OVITO [6], an analysis was made of the amounts and percentage of different types of unit cells in the structure of the sample at successive times of SH-synthesis. The analysis showed that over time (after the relaxation and warm-up stages of the initial SHS-sample zone, when the SHS process is initiated), the number of bcc structures is increasing and the number of fcc and hcp structures is decreasing, the number of structures type "icosahedron" (ico) is negligible (less than 0.1%).

Computer simulation of SH-synthesis of NiAl by the MDS method in the LAMMPS package using parallel computations was carried out on 3 computational platforms:

1. Computational cluster "RAMEC" of Altai State University (32 computational nodes). Characteristics of the computing unit: 4-core Intel i7-3820 processor (8 streams), 8 GB RAM, 3 GPUs AMD Radeon R7370;
2. A computer with a 6-core Intel i7-3930K processor (12 streams), 32 GB of RAM, 2 video cards: NVidia Tesla C2050 and Nvidia Quadro 600;
3. Cluster of workstations (15 PCs) - local area network. Each PC has a 4-core Intel i5-7400 processor, 4 GB RAM.

3. Conclusion
The ability to parallelize the calculations significantly reduces the computation time spent on both one and the entire CEs cycle and improves the efficiency of multi-scale predictive SHS simulation, allows for correctly taking into account the influence of processes occurring at the nano-, micro- and mesolevels of the structural and functional hierarchy of heterogeneous systems on the processes occurring at its macrolevel and, therefore, more accurately to predict the structure and properties of the SHS target products. The possibility of studying the regime of microheterogeneous combustion and on this basis recognizing the local instability of the motion of the combustion wave makes it possible to timely control the SHS process to ensure its stability and uniformity throughout the volume.

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4. References
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