The influence of the initiation's conditions of the SH-synthesis of intermetallic compounds on the combustion parameters of the nanoscale layered composition Ti-15.82wt.%Al

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Abstract. Computational experiments (CEs) have been carried out to simulate the propagation of the combustion wave of the SH-synthesis process in a package of alternating layers of nanoscale crystal lattices of Ti and Al atoms by molecular dynamics method. In the LAMMPS package was used the interatomic interaction potential in the embedded atom model (EAM). Using the LAMMPS configuration with parallel computing, the following results of CEs were obtained: sets of temperature profiles along the layers of the structure at successive instants of time (up to 16 ns) and a corresponding sets of snapshots (vertical cross-sections of the atomic arrangement along the layers), as well as a table with the number and percentage of the content of various types of elementary cells (fcc, hcp, bcc, other) at the same instants of time. The influence of the initiation's conditions of the SH-synthesis of intermetallic compounds on the combustion parameters of the nanoscale layered composition Ti-15.82wt.%Al was showed.

1. Introduction

One of the effective methods for obtaining modern functional materials with predetermined properties is the method of "self-propagating high-temperature synthesis (SHS)", in which reagents are used in the form of fine powders, thin films, liquids, gases, etc. In the pressed sample, an exothermic reaction combustion in a thin layer of interacting reagents, which spontaneously propagates through the sample by heat transfer from layer to layer. The products of SHS are characterized by a variety of micro-, meso- and macrostructures, which largely depends on the initial structure of the packing of the particles 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 behavior of the front of the combustion wave (on the stability of the front motion) is affected by the inhomogeneous, to some extent, random 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 problem of analyzing the microheterogeneous structure of the combustion wave (with the presence of isolated microvolumes of self-ignition in the combustion wave structure) was called the SHS "discreteness problem", and in most cases it is solved experimentally because the conclusions of various theoretical models on the behavior of the combustion wave at a macroscopic and / or microscopic level contradict each other.

To study the combustion kinetics of dispersive-phase systems and the evolution of the discrete decay of the thermal structure of the SHS wave in locally unstable modes of microheterogeneous combustion, it is necessary to thoroughly study and refine the physicochemical and mathematical model concepts of various structural and phase transformations in the SH-synthesis process. These

model concepts plays an important role in optimizing technological modes of SH-synthesis of materials with specified functional and operational properties.
In this paper, some model concepts of the microheterogeneous combustion regime during the SHS process in the model "layered" structures of the Ti-Al powder mixture (figure 1) are considered, the composition of the components in it correspond to certain stoichiometric relationships. The study of the microheterogeneous combustion regime in the course of the SHS process in the model "layered" structures of the mixture is carried out by computer simulation using the "molecular dynamics (MD)" method in the LAMMPS package, using its possibility of parallel computations [1].
The adequacy of the molecular dynamic simulation of the SH-process microkinetics in layered atomic structures requires the creation of a computational structure with an amount from 500,000 to several million atoms and a study time range of at least 15 ns. Computational experiments on the simulation of the SH-process microkinetics, the results of which are reflected in this work, were performed on a cluster of workstations (15 PCs) - local area network. Each PC has a 4-core Intel i5-7400 processor, 4 GB RAM. One computational experiment performed on the above-mentioned cluster using the LAMMPS package in the parallel computing mode takes about 6-7 days. For a comprehensive study of the SH-process, at least a dozen such computational experiments are required. Therefore, under these conditions, the use of parallel computing is a necessary.
The possibility of studying the regime of microheterogeneous combustion and on this basis of recognizing the local instability of motion of the combustion wave makes it possible to timely control the SHS process to ensure its stability and homogeneity throughout the bulk of the powder mixture. This aspect of the task is relevant and important in the practical application of SHS for the development of 3D printers of finished products from metal and cermets in the field of additive technologies. The main controlled parameters are the temperature and propagation velocity of the SHS combustion wave along the molded powder mixture of the initial reagents.

2. The stages of molecular-dynamic simulation of SH-synthesis of intermetallic compounds of system Ti-Al in the LAMMPS package using parallel computations

The MD method realizes a discrete-continual simulation approach: Newtonian mechanics is used as the basis for describing the time evolution of the system, and the system itself is represented as a collection of particles (as material points). The process is simulated by integrating the equations of motion of individual particles on the basis of a simple potential interaction with a constant time step. Simulation by the MD method of the evolution of a system of "large" particles (individual granules of a material) gives its macroscopic description, and in the case of simulation at the atomic level, quantum effects are encapsulated in a potential function to refine the features of the interaction of particles in the system. 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 MD 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.
Simulation of the combustion wave propagation during the SH-synthesis of intermetallic compounds of Ti-Al system was performed using the MD method in the LAMMPS package supporting parallel computations.
In the initial layered structure of the Ti-Al system (fig. 1), each "large" layer of the structure consists of several atomic planes forming a crystal structure (lattice) of elementary crystalline cells.
The cells of Ti have hcp type with the parameters: parameter a = 0.29508 nm and c = 0.46855 nm [2]. The cells of Al have fcc type with parameter a = 0.405 nm [3, 4]. The composition Ti-15.82wt.%Al correspond to Ti-25vol.%Al. The ratio of the number of atoms is N_{Ti}/N_{Al} = 3, i.e. the fraction of Ti atoms is equal to n = 0.75 (75%) and the fraction of Al atoms is equal 0.25 (25%).

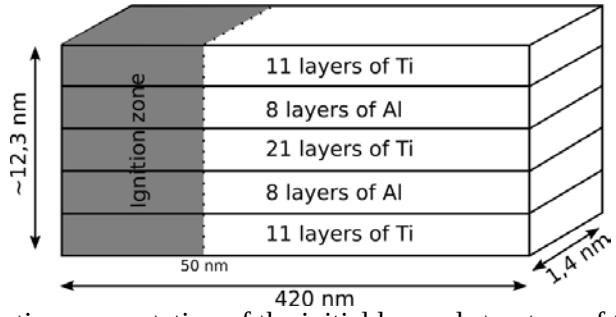

Figure 1. Schematic representation of the initial layered structure of the Ti-Al system.

The initial temperature of the sample (fig. 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=414956, 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.

At this stage, within 0.1 ns, the structure is heated in the initial region of the sample (50x1.4x12.3 nm) under the conditions of the NVT ensemble, where V is the volume of the heating region. In first case, the structure is heated from 600 to 1200 K, and in second case – from 600 to 1400 K. During this same period of time for the system of atoms in the remaining region of the sample with dimensions (370x1.4x12.3 nm) the conditions of the NVE ensemble (E-total energy of the atoms) are established. Then is started the simulation of the propagation of the SH-synthesis wave with the preservation of the conditions of the NVE ensemble for the whole sample. At the same time, "free" boundary conditions are imposed on the boundaries of the calculated region along the X axis, and periodic boundary conditions remain along the Y and Z axes.

In the computational experiments (CEs) on simulation of the Ti-Al system evolution was used the interatomic interaction potential (fig. 2) in the "embedded atom model (EAM)" [2].

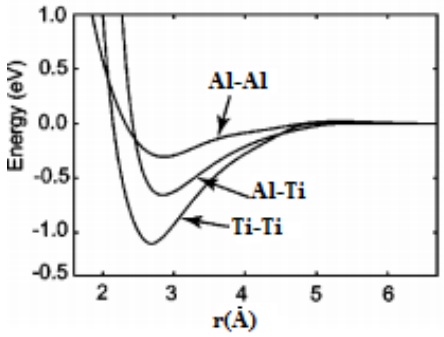

Figure 2. Pair-interaction function for the Ti-Al system in the effective pair format [2].

Using the given EAM-potential of the 2003-th year (designated EAM_2003), correct results were obtained in [2] not only for the synthesis of the γ-TiAl intermetallic compound, but also for the Ti_3Al and $TiAl_3$ intermetallic compounds. The observed agreement with experimental data [2] demonstrates good transferability of this potential EAM_2003. The EAM_2003 potential correctly predicts the lattice constants, cohesive energy, and elastic constants.

According to figures 3(a) and 3(b), in first case, the structure is heated from 600 to 1200 K, and in second case – from 600 to 1400 K.

By means of the boundaries of the "plateau" of each temperature profile (fig. 3(a),(b)) with use of the EAM_2003 potential was estimated the velocity of the combustion wave front, that is decreased approximately from 6 m/s (time range 4-8 ns) to 2 m/s (time range 12-16 ns).

Thus, the combustion kinetics for micro- and nanosized samples of layered structures (nanofoils) develops two orders of magnitude faster than in macrosized samples. However, the values of the velocity for SH-synthesis in the Ni-Al system under similar conditions are significantly higher (about 30 m/s, [5-8]).

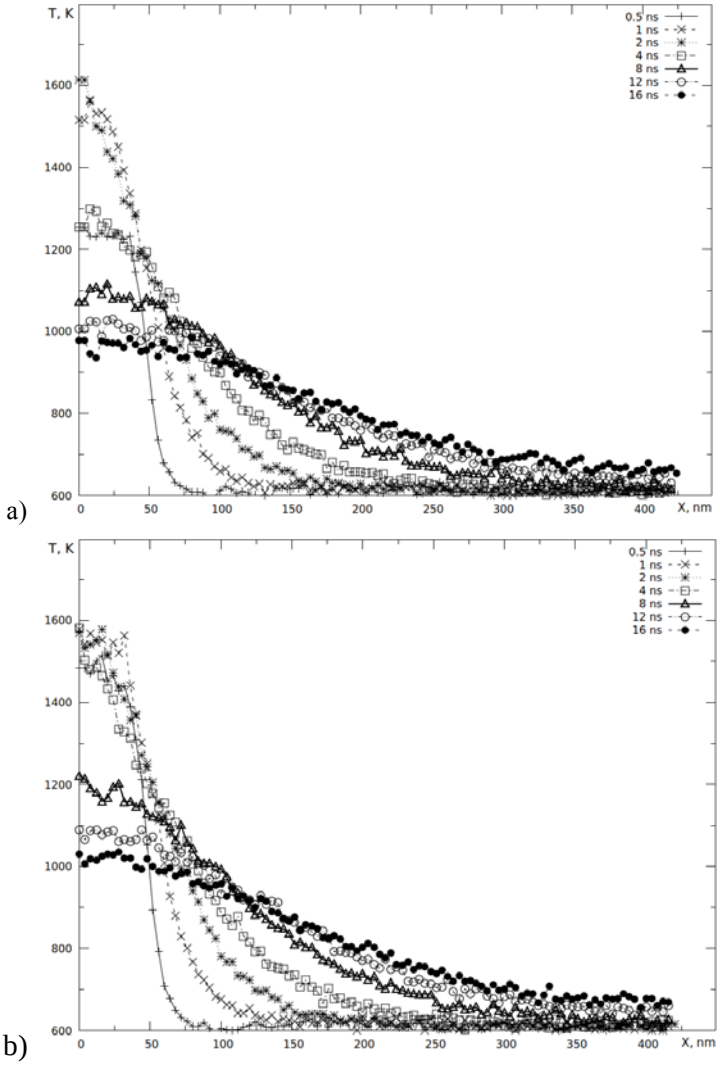

Figure 3. Sets of temperature profiles as functional dependencies of the combustion temperature of SHS vs. the coordinate X for consecutive moments of time: a) the heating in the initial region of the sample (50x1.4x12.3 nm) from 600 to 1200 K; b) the heating in the initial region of the sample (50x1.4x12.3 nm) from 600 to 1400 K.

For two modes of heating the sample initial zone, a difference is observed in the combustion temperatures in the time range from 2 ns to 8 ns, but then the temperature profiles rapidly approach each other (the SHS reaction tends to fade). The combustion temperature in both cases decreases to the melting point of Al. Under such initial conditions for the initiation of the SH-synthesis of intermetallic compounds of the Ti–Al system in real experiments, taking into account the presence of the porosity of the mixture, the synthesis reaction transiently ceases. Therefore, in further computational experiments, the values of the initial temperature of SHS ignition will be increased.

Using the software package OVITO [9], designed to recognize and visualize the structures of elementary cells (fcc, bcc, hcp, ico and other) in simulated atomic and molecular systems, an analysis was carried out of the amounts and percentage of different types of unit cells in the structure of the sample at consecutive times of SH-synthesis (fig. 4 and fig. 5). The heating of the sample initial zone from 600 to 1200 K correspond to figures 4 and 5.

The Ackland-Jones bond-angle method (modifier of OVITO package, [10]) was used for recognition of unit cell types (fig. 5). Figure 5, taking into account the sample length of 420 nm, allows us to obtain the same estimates of the SHS reaction velocity, which are given above and were obtained using temperature profiles (fig. 3(a), (b)).

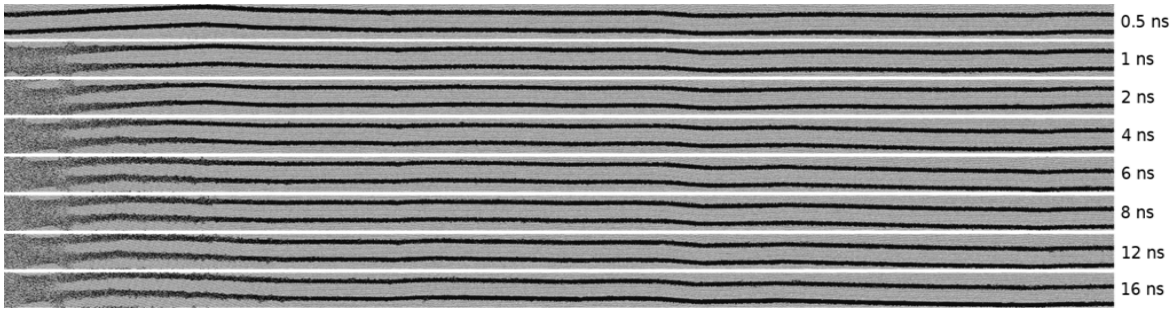

Figure 4. Set of the microsections (snapshots) of the distribution structure of Ti atoms (tint of light grey) and Al atoms (black dots) along the sample at successive instants of time: the homogeneous zone (tint of dark grey) at the beginning of the sample (on the left) corresponds to the phase formation of intermetallic compounds (1-16 ns).

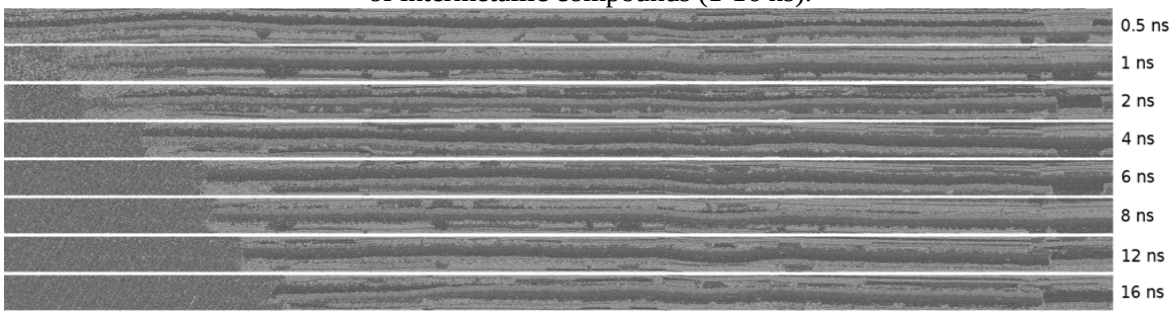

Figure 5. Set of the microsections (snapshots) of the distribution structure of various types of elementary cells along the sample at the successive instants of time: fcc – tint of light grey (0.5 – 16 ns); bcc – the homogeneous zone (grey tint of middle degree) at the beginning of the second snapshot (1 ns, on the left); hcp – the homogeneous zones (tint of dark grey) on the snapshots (2 – 16 ns, on the left) and continuous strips along the whole snapshots (0.5 - 16 ns).

With a careful analysis of figures 4 and 5 it can be stated that the boundaries of the motion of the combustion front, reflected in both figures, correspond to each other.

Within the time range of up to 2 ns, the combustion temperature (fig. 3a) rises to approximately 1550 K (above the melting point of the Ti_3Al compound), therefore, $TiAl_3$ and TiAl compounds can be formed with the exception of the Ti_3Al compound. The homogeneous zone, reflected on the figure 5 at the beginning of the second snapshot (1 ns, on the left) with grey tint of middle degree, in the OVITO package was colored in blue corresponding to the bcc structures. Of the two intermetallic compounds mentioned above, the structure of the $TiAl_3$ compound is close to the bcc structure, and the structure of the TiAl compound is close to the fcc structure (in the OVITO package was colored in green, on the figure 5 – tint of light grey). In the following instants of time the blue color reflected by OVITO was noticeably reduced (in the figure 5 in the beginning of the next snapshots was appeared the tint of dark grey corresponding to the hcp structures, i.e. to the Ti_3Al compound). This is explained by the reaction of the $TiAl_3$ compound with Ti atoms and the formation of the Ti_3Al compound, accompanied by a decrease in the combustion temperature (fig. 3(a)) below the melting point of Ti_3Al, thereby ensuring the phase formation of the Ti_3Al compound.

The percentage of intermetallic compounds indicated in the table below confirms the predominance of the compounds Ti_3Al and TiAl in the simulated sample structure.

3. Conclusion

Computer simulation of SH-synthesis of intermetallic compounds of system Ti-Al by the MDS method in the LAMMPS package using parallel computations was carried out on the cluster of workstations (15 PCs) - local area network. Each PC has a 4-core Intel i5-7400 processor, 4 GB RAM. 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. The general conclusion from the results of computational experiments is as follows.

Table. The number and percentage of different types of unit cells in the structure of the sample at consecutive times of SH-synthesis.

Time, ns	FCC	HCP	BCC	ICO	Other
0.5	177462 (42.8 %)	197697 (47.6 %)	11944 (2.9 %)	213 (0.1 %)	27640 (6.7 %)
1	183279 (44.2 %)	187974 (45.3 %)	14484 (3.5 %)	278 (0.1 %)	28943 (7.0 %)
2	188299 (45.4%)	187590 (45.2 %)	14388 (3.5 %)	149 (<0.1 %)	24530 (5.9 %)
4	190222 (45.8 %)	188601 (45.5 %)	13655 (3.3 %)	111 (<0.1 %)	22367 (5.4 %)
6	190277 (45.9 %)	190928 (46.0 %)	13069 (3.1 %)	105 (<0.1 %)	20577 (5.0 %)
8	190246 (45.8 %)	192053 (46.3 %)	12778 (3.1 %)	84 (<0.1 %)	19795 (4.8 %)
12	187870 (45.3 %)	194775 (46.9 %)	12238 (2.9 %)	82 (<0.1 %)	19991 (4.8 %)
16	185885 (44.8 %)	197327 (47.6 %)	12331 (3.0 %)	92 (<0.1 %)	19321 (4.7 %)

For initial temperature of the sample 600 K and two modes of heating the sample initial zone (from 600 to 1200 K and from 600 to 1400 K) the SHS reaction tends to fade (fig. 3(a) and fig. 3(b)). The combustion temperature in both cases decreases to the melting point of Al. Therefore, in further computational experiments, the values of the initial temperature of SHS ignition will be increased.

4. References

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