The influence of the ignition conditions of the SH-synthesis of intermetallic compounds on the combustion parameters of the Ti-15.82wt.%Al composition: computer simulation and computing experiments

V I Jordan and I A Shmakov

Altai State University, Lenina ave., 61, Barnaul, Russia, 656049

e-mail: jordan@phys.asu.ru, ihammers.sia@gmail.com

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. The interatomic interaction potential in the embedded atom model (EAM) was used in the LAMMPS package. 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 the corresponding sets of snapshots (vertical cross-sections of the atomic arrangement along the layers), as well as a tables 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 Ti-15.82wt.%Al composition was showed. The ignition conditions of SHS that are provided the stable motion of the combustion wave in the SHS-sample were determined. And the ignition conditions of SHS with dominance of either TiAl or Ti3Al phase formation in the SHS products was also determined.

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, etc. In the pressed sample, the exothermic reaction combustion 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 the combustion wave propagation 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 play an important role in optimizing technological modes of SHS-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 (MDS) 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 of time SHS process 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 cermet 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 titanium-aluminum compounds 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 system time evolution, and the system itself is represented as a collection of particles (as material points). The process is simulated by integrating the equations of individual particles motion 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 particle interaction 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 (figure 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 $a = 0.29508\,\text{nm}$ and $c = 0.46855\,\text{nm}$ [2]. The cells of Al have fcc type with parameter $a = 0.405\,\text{nm}$ [3, 4]. The Ti-15.82wt.%Al composition correspond to Ti-25vol.%Al. The ratio of the number of atoms is $N_{\text{Ti}}/N_{\text{Al}} = 3$, 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.](image)

The initial temperature of the sample (figure 1) is assumed to be 700 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 $P=1\,\text{Bar}$, and the temperature $T=700\,\text{K}$ (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 700 to 1200 K, and in second case – from 700 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 the simulation of the propagation of the SH-synthesis wave is started 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 (figure 2) in the "embedded atom model (EAM)" [2].

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

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$_3$Al 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.

3. The analysis of molecular-dynamic simulation results of SH-synthesis of intermetallic titanium-aluminum compounds

According to figures 3(a) and 3(b), in first case, the SHS-sample is heated from 700 to 1200 K, and in second case – from 700 to 1400 K.
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 700 to 1200 K; b) the heating in the initial region of the sample (50x1.4x12.3 nm) from 700 to 1400 K.

By means of the boundaries of the "plateau" of each temperature profile (figures 3(a),(b)) with use of the EAM_2003 potential the velocity of the combustion wave front was estimated, 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]).

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 rapidly 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 (figures 4(a) and 4(b)). The heating of the sample initial zone from 700 to 1200 K correspond to figure 4(a) and the heating of the sample initial zone from 700 to 1400 K correspond to figure 4(b).
Figure 4. Sets of the microsections (snapshots) of the distribution structure of various types of elementary cells along the SHS-sample at the successive instants of time: fcc – green dots on the snapshots; bcc – blue dots at the beginning of the snapshots (0.5 – 4 ns, on the left); hcp – red dots on the snapshots: a) - the heating of the sample initial zone from 700 to 1200 K; b) - the heating of the sample initial zone from 700 to 1400 K.

The Ackland-Jones bond-angle method (modifier of OVITO package, [10]) was used for recognition of unit cell types (figures 4(a) and 4(b)). Figures 4(a) and 4(b), 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 (figures 3(a), (b)).

Within the time range of up to 2 ns, the combustion temperature (figures 3(a) and 3(b)) rises to approximately 1550 K (above the melting point of the Ti3Al compound), therefore, TiAl3 and TiAl compounds can be formed with the exception of the Ti3Al compound. The zone with blue dots, reflected on the figure 4(a) in the beginning of the second snapshot (1 ns, on the left) and on the figure 4(b) of the snapshots (1, 2 and 4 ns, on the left), correspond to the bcc structures. Of the two intermetallic compounds mentioned above, the body-centered tetragonal (bct) structure of the TiAl3 compound is close to the bcc structure (on the figures - blue dots), and the face-centered tetragonal (fct) structure of the TiAl compound is close to the fcc structure (on the figures - green dots). In the following instants of time the blue color in the beginning of the next snapshots of the figures 4(a) and 4(b) was noticeably reduced (TiAl3 compound percentage was noticeably reduced), but was appeared the red tint corresponding to the hcp structures (i.e., corresponding to the Ti3Al compound). This is explained by the reaction of the TiAl3 compound with Ti atoms (after the time interval of superadiabatic heating) and the formation of the Ti3Al compound, accompanied by a decrease in the combustion temperature below the melting point of Ti3Al (figures 3(a) and 3(b)), thereby ensuring the phase formation of the Ti3Al compound.

For initial temperature of the sample 700 K and two modes of heating the sample initial zone (from 700 to 1200 K and from 700 to 1400 K) the SHS reaction tends to fade (figures 3(a) and 3(b)). The combustion temperature in both cases decreases to the melting point of Al. 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 also tends to fade (therefore the analogous figures was not showed). Therefore, in further computational experiments, the values of the initial temperature of SHS ignition have been increased. According to figures 5(a) and 5(b), in the first case, the SHS-sample is heated from 800 to 1200 K and in the second case – from 800 to 1300 K.

Figures 5(a) and 5(b) show that superadiabatic heating in the first nanoseconds for the second case (the heating from 800 to 1300 K) occurs noticeably faster and the maximum superadiabatic temperature is higher than for the first case (the heating from 800 to 1200 K).
Figure 5. 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 800 to 1200 K; b) the heating in the initial region of the sample (50x1.4x12.3 nm) from 800 to 1300 K.

However, the combustion temperature for the first case is more than 100 K higher than the second case and for the first case in the practical sense a “temperature plateau” is observed on the temperature profiles (figure 5(a)).

In addition, the combustion front motion velocity for the first case is stable and is approximately equal to 18-19 m/s. For the second case of SHS ignition (the heating from 800 to 1300 K), the combustion front motion velocity gradually decreases with time (from about 18 to 12 m/s) and it is difficult to speak about the “temperature plateau” (figure 5(b)).

Analysis of the both microsections (snapshots) sets of the distribution structure of various types of elementary cells (figures 6(a) and 6(b)) shows that before the appearance of intermetallic phases TiAl (green dots) and Ti$_3$Al (red dots) first appears the phase TiAl$_3$ (blue dots) at the interfaces of the contacting Ti and Al layers in the zones reached by the combustion front. There is a clear dominance of the TiAl phase in the products of the SHS reaction in the first case of the ignition of SHS (figure 6(a) - the heating from 800 to 1200 K). And vice there is a clear dominance of the Ti$_3$Al phase in the products of the SHS reaction in the second case (figure 6(b) - the heating from 800 to 1300 K).

The percentage of intermetallic compounds indicated in the tables 1 and 2 below confirms the predominance of the TiAl compound in the SHS products in the first case and Ti$_3$Al - in the second case. According to the table 1, the percentage of the TiAl compound (the fct structure that is close to the fcc structure) increases from 42.6 to 64.2 % (the percentage of the Ti$_3$Al compound with hcp structure type decreases from 44.5 to 17.3 %). According to the table 2, the percentage of the Ti$_3$Al
The percentage of the TiAl compound decreases from 43.0 to 24.5%.

**Figure. 6.** Sets of the microsections (snapshots) of the distribution structure of various types of elementary cells along the SHS-sample at the successive instants of time: fcc – green dots on the snapshots; bcc – blue dots at the beginning of the snapshots (0.5 – 4 ns, on the left); hcp – red dots on the snapshots: a) - the heating of the sample initial zone from 800 to 1200 K; b) - the heating of the sample initial zone from 800 to 1300 K.

**Table 1.** The number and percentage of different types of unit cells in the structure of SHS-sample at consecutive times (the heating from 800 to 1200 K).

| Time, ns | FCC   | HCP   | BCC   | ICO   | Other |
|----------|-------|-------|-------|-------|-------|
| 0.5      | 176650| 184845| 19292 | 235   | 33934 |
|          | (42.6%)| (44.5%)| (4.6%)| (0.1%)| (8.2%)|
| 1        | 175355| 180711| 22055 | 435   | 36400 |
|          | (42.3%)| (43.5%)| (5.3%)| (0.1%)| (8.8%)|
| 2        | 179703| 176552| 23204 | 322   | 35175 |
|          | (43.3%)| (42.5%)| (5.6%)| (0.1%)| (8.5%)|
| 4        | 185815| 168447| 25786 | 267   | 34641 |
|          | (44.8%)| (40.6%)| (6.2%)| (0.1%)| (8.3%)|
| 6        | 195586| 155456| 28010 | 269   | 35635 |
|          | (47.1%)| (37.5%)| (6.8%)| (0.1%)| (8.6%)|
| 8        | 203848| 142653| 30538 | 275   | 37642 |
|          | (49.1%)| (34.4%)| (7.4%)| (0.1%)| (9.1%)|
| 12       | 238638| 102564| 34572 | 258   | 38924 |
|          | (57.5%)| (24.7%)| (8.3%)| (0.1%)| (9.4%)|
| 16       | 266494| 71766 | 36275 | 191   | 40230 |
|          | (64.2%)| (17.3%)| (8.7%)| (<0.1%)| (9.7%)|

4. **Conclusion**

Computer predictive simulation of SHS microkinetics in the Ti-15.82 wt.%Al composition (the stoichiometric ratio of the number of atoms is $N_{Ti}/N_{Al}=3$) by the MDS method in the LAMMPS package using parallel computations was carried out. The parallel computations have significantly reduced the total computation time.

The ignition conditions of SHS that are provided the stable motion of the combustion wave in the SHS-sample were determined. And the ignition conditions of SHS with dominance of either TiAl or
Ti₃Al phase formation in the SHS products was also determined. The recognizing the local instability of the combustion wave makes it possible to timely control the SHS process throughout the volume.

### Table 2

The number and percentage of different types of unit cells in the structure of SHS-sample at consecutive times (the heating from 800 to 1300 K).

| Time, ns | FCC    | HCP    | BCC    | ICO    | Other  |
|---------|--------|--------|--------|--------|--------|
| 0.5     | 178442 | 181251 | 19847  | 321    | 35095  |
|         | (43.0 %) | (43.7 %) | (4.8 %) | (0.1 %) | (8.5 %) |
| 1       | 158646 | 195170 | 22033  | 430    | 38677  |
|         | (38.2 %) | (47.0 %) | (5.3 %) | (0.1 %) | (9.3 %) |
| 2       | 147772 | 205551 | 23335  | 449    | 37849  |
|         | (35.6 %) | (49.5 %) | (5.6 %) | (0.1 %) | (9.1 %) |
| 4       | 128049 | 227892 | 23538  | 446    | 35031  |
|         | (30.9 %) | (54.9 %) | (5.7 %) | (0.1 %) | (8.4 %) |
| 6       | 121343 | 234656 | 24271  | 397    | 34289  |
|         | (29.2 %) | (56.5 %) | (5.8 %) | (0.1 %) | (8.3 %) |
| 8       | 109710 | 242865 | 25307  | 500    | 36574  |
|         | (26.4 %) | (58.5 %) | (6.1 %) | (0.1 %) | (8.8 %) |
| 12      | 99262  | 251047 | 26096  | 514    | 38037  |
|         | (23.9 %) | (60.5 %) | (6.3 %) | (0.1 %) | (9.2 %) |
| 16      | 101533 | 249672 | 26658  | 397    | 36696  |
|         | (24.5 %) | (60.2 %) | (6.4 %) | (0.1 %) | (8.8 %) |

### 5. References

[1] Plimpton S 1995 J. Comp. Phys. 117(1) 1-19

[2] Zope Rajendra R, Mishin Y 2003 Phys. Rev. B 68 024102

[3] Mishin Y, Mehl M J and Papaconstantopoulos D A 2002 Phys. Rev. B. 65(22) 224114

[4] Purja Pun G P, Mishin Y 2009 Philosophical Magazine 89(34-36) 3245-3267

[5] Shmakov I A, Jordan V I and Sokolova I E 2018 High-Performance Computing Systems and Technologies 8(1) 48-54

[6] Turlo V, Politano O and Baras F 2015 Acta Materialia 99 363-372

[7] Rogachev A S 2016 Combustion and Flame 166 158-169

[8] Baras F, Politano O 2018 Acta Materialia 148 133-146

[9] Stukowski A 2010 Modelling and Simulation in Materials Science and Engineering 18 015012

[10] Ackland G J, Jones A P 2006 Phys. Rev. B 73(5) 054104

### Acknowledgments

The reported study was funded by RFBR according to the research projects No. 18-41-220004 and No. 18-08-01475.