Reproducibility of a heterophase structure emergence effect when changing the ignition temperature of SHS in a layered nanosized nonstoichiometric Ti-Al system

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Abstract. The simulation results of SHS process in a package of alternating nanoscale layers of the crystal lattices of Ti and Al atoms for two systems with various numbers of atoms and nonstoichiometric ratios are given. For simulation the LAMMPS package supporting parallel computations and the interatomic interaction potential in the “embedded atom” model (EAM) have been used. For two systems with various numbers of atoms and nonstoichiometric ratios the sets of temperature and density profiles along the layers of the structure at successive instants of time (up to 16 ns) have been obtained. For a system with 453974 atoms and a nonstoichiometric ratio of 1.23 the heterostructure emergence with an alternation of intermetallic phases when changing the SHS “ignition” temperature has been reproduced.

1. Introduction
In this paper, some model concepts of the microheterogeneous combustion in the process of the "self-propagating high-temperature synthesis (SHS)" in the model "layered" structures of the Ti-Al systems (figure 1) are considered. The compositions of the components in these systems correspond to certain nonstoichiometric ratios. The study of the microheterogeneous combustion regime in the model "layered" structures of the Ti-Al system is carried out by computer simulation using the "molecular dynamics (MD)" method in the LAMMPS package supporting parallel computations [1]. The study can be used to simulate nanoobjects in order to study their properties and to find methods of synthesis.

![Figure 1](image-url)

Figure 1. Schematic representation of the initial layered structures of the Ti-Al systems: (a) – $N_{Ti}/N_{Al} = 1.15$, $N_{Ti}=936998$; (b) – $N_{Ti}/N_{Al} = 1.23$, $N_{Ti}=453974$. 

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Each "large" layer of the structures in the Ti-Al systems (figure 1) consists of several atomic planes forming a crystal structure of elementary cells. The cells of Ti correspond to hcp type and the cell parameters are as follows: \( a = 0.29508 \) nm, \( c = 0.46855 \) nm [2]. The cells of Al correspond to fcc type and the cell parameter \( a \) is equal 0.405 nm [3, 4]. In the first system with 936998 atoms (figure 1(a)) the nonstoichiometric ratio is \( N_{\text{Ti}}/N_{\text{Al}} = 1.15 \), i.e. the fraction of Ti atoms is equal to \( n = 0.535 \) (53.5 %) and the fraction of Al atoms is equal to 0.465 (46.5 %). In the second system with 453974 atoms (figure 1(b)) the nonstoichiometric ratio is \( N_{\text{Ti}}/N_{\text{Al}} = 1.23 \), i.e. the fraction of Ti atoms is equal to \( n = 0.552 \) (55.2 %) and the fraction of Al atoms is equal to 0.448 (44.8 %). The initial temperature for the both Ti-Al systems is assumed to be 800 K, and at this temperature the entire structures were "relaxed" for 0.4 ns with fixed thermodynamic parameters (NPT-ensemble): a) the external pressure \( P = 1 \) Bar; b) the temperature \( T=800 \) K. The periodic boundary conditions were established for all 3 dimensions at this stage of the simulation.

Periodic boundary conditions are also preserved for the entire sample at the next stage. At this stage the both systems are heated from 800 to 1400 K within 0.1 ns in the initial regions (50x1.4x27.5 nm and 50x1.4x13.5 nm, respectively) under the conditions of the NVT ensemble, where \( V \) is the volume of the heating region. The conditions of the NVE ensemble (E-total energy of the atoms) are established during this same period of time for the both systems in the remaining regions with dimensions 370x1.4x27.5 nm and 370x1.4x13.5 nm, respectively. Afterwards the simulation of the propagation of the SH-synthesis wave with the preservation of the conditions of the NVE ensemble for the whole volume of the each Ti-Al system is being carried out. At the same time the "free" boundary conditions are imposed on the boundaries of the calculated region along the X axis and periodic boundary conditions are remained along the Y and Z axes.

2. The computational experiments on the simulation of the Ti-Al system evolution
In the computational experiments (CEs) the interatomic interaction potential in the "embedded atom model (EAM)" of the 2003-th year (designated EAM_2003) [2] was used. By means of the boundaries of the "plateau" of each temperature profile (figures 2, 3) using the EAM_2003 potential, the velocity of the combustion wave front (approximately 18 m/s in the first and 19–20 m/s in the second systems) was estimated. However, the values of the velocity for SH-synthesis in the Ni-Al system under similar conditions proved to be significantly higher (about 30 m/s, [5–8]).

Thus, the combustion kinetics for micro- and nanosized systems with layered structures (nanofoils) develops two orders of magnitude faster than in macrosized systems, since the specific surface for nanoscale structures (greater than 20 m²/g) is more than two orders of magnitude greater than for porous macrostructures (from 0.1 to 2 m²/g). In the first system the combustion temperature is equal to 1470–1490 K and in the second system is equal to 1490–1500 K.

Figure 2. Sets of temperature profiles as functional dependencies of the combustion temperature of SHS vs. the coordinate X for consecutive moments of time: the heating from 800 to 1400 K in the initial regions of the first (a) and of the second (b) systems.
**Figure 3.** Sets of temperature profiles as functional dependencies of the combustion temperature of SHS vs. the coordinate X for consecutive moments of time; the heating in the initial region of the second system: (a) from 800 to 1300 K; (b) from 800 to 1200 K.

The combustion temperature of 1470–1500 K (figures 2, 3) is above the melting point of the Ti₃Al compound, therefore Ti₃Al and TiAl compounds can be formed with the exception of the Ti₃Al compound. Body-centered tetragonal (bct) structure of the Ti₃Al compound is close to the bcc structure (her blue dots are dominant in the composition of lilac shade in figures 4, 5), and the face-centered tetragonal (fct) structure of the TiAl compound is close to the fcc structure (green dots – her dots in the composition of lilac shade in figures 4, 5).

**Figure 4.** Set of the microsections (snapshots) of the distribution structure of various types of elementary cells along the first system at the successive instants of time: red dots – hcp type (Ti cells), green dots – fcc type (Al cells), blue dots – bcc type; the heating from 800 to 1400 K in the initial region of the first system.

**Figure 5.** Set of the microsections (snapshots) of the distribution structure of various types of elementary cells along the second system at the successive instants of time: red dots – hcp type (Ti cells), green dots – fcc type, blue dots – bcc type; the heating from 800 to 1400 K in the initial region of the second system.

The software package OVITO and the Ackland-Jones bond-angle method (modifier of OVITO package, [9]) for the recognition and visualization of the elementary cells in the structures of the both
systems have been used. Taking into account the equal structure length of 420 nm for the both systems and using the figures numbered from 4 to 6, the recognition of unit cell types (figure 4, 5) and estimation of the SHS reaction velocity have been carried out. The SHS reaction velocity is equal to 18 m/s for the first system and for the second system is equal to 19–20 m/s (the same results are obtained using figures 2, 3). The density of the first system by the end of 16 ns in according to the propagation zone of the combustion wave (figure 6(a)) is approximately equal to 3.32–3.34 g/cm$^3$ and this value is in the density range of 3.15–3.38 g/cm$^3$, corresponding to TiAl$_3$ compound.

**Figure 6.** Sets of density profiles as functional dependencies of the density of the both systems vs. the coordinate X for consecutive moments of time: the heating from 800 to 1400 K in the initial regions of the first system (a) and the second system (b).

During the time interval from 8 to 16 ns as result of the propagation of the SH-synthesis wave in the second system the heterophase structure has been emerged (figures 5, 6(b)). As can be seen from figures 5 and 6(b), by the end of 16 ns, at least three zones with sharp rectilinear boundaries appear (in them green dots dominate in relation to a small quantity of blue dots). The dominance of green dots (fcc type) with respect to blue dots (bcc type) in these three zones confirms the dominance of the TiAl phase (its fct type is close to fcc) in relation to the TiAl$_3$ phase (its bct type is close to bcc). Unit cells of Al correspond to the fcc type (green dots), but in three zones there can be no phase of liquid Al, since in figure 5 there is no clearly defined green color tone in the corresponding zones. In addition, in the density profiles (figure 6(b)) in the corresponding zones, an increased density of 3.5 g/cm$^3$ is observed instead of a lower value of 2.3–2.4 g/cm$^3$, which is characteristic of the density of liquid Al.

The heterophase structure emergence effect is stably reproduced even with a change (decrease) in the initial temperature of the ignition of the SHS (figures 7–9). The emergence of a heterophase structure is most likely due to a certain range of the nonstoichiometric ratio (near 1.23–1.25) and the ratio of the thicknesses of the Ti and Al layers in the original Ti-Al system.

**Figure 7.** Set of the microsections (snapshots) of the distribution structure of various types of elementary cells along the second system at the successive instants of time: red dots – hcp type (Ti cells), green dots – fcc type, blue dots – bcc type; the heating from 800 to 1300 K in the initial region of the second system.
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Figure 8. Set of the microsections (snapshots) of the distribution structure of various types of elementary cells along the second system at the successive instants of time: red dots – hcp type (Ti cells), green dots – fcc type, blue dots – bcc type; the heating from 800 to 1200 K in the initial region of the second system.

Figure 9. Sets of density profiles as functional dependencies of the density of the second system vs. the coordinate X for consecutive moments of time. The heating in the initial region of the second system: (a) – from 800 to 1300 K; (b) – from 800 to 1200 K.

3. Conclusion
The elucidation of the causes of the heterophase structure emergence in the SHS requires further research. Computer simulation of SH-synthesis in the Ti-Al system by the MD method in the LAMMPS package using parallel computations was carried out on the cluster of workstations (15 PCs) that is local area network. Each PC has a 4-core Intel i5-7400 processor, 4 GB RAM.

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