The emergence of a heterostructure of the intermetallic phases in the process of SH-synthesis simulation in a nonstoichiometric nanoscale layered Ti-Al system

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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 nanosized layers of crystal lattices of Ti and Al atoms by the «molecular dynamics» method. By means of the LAMMPS package performing parallel computing the computational experiments (CEs) have been carried out. The “embedded atom” model (EAM) for the interatomic interaction potential was used. The two structures of Ti-Al system with various quantities of atoms and nonstoichiometric ratios have been studied. The sets of temperature and density profiles along the layered structure at successive instants of time (up to 16 ns) have been calculated. In addition, the corresponding sets of vertical cross-sections of the distributions of atoms and various types of elementary cells (fcc, hcp, bcc, etc.) have been calculated. The emergence of heterostructure of intermetallic phases in the Ti-Al system with 453974 atoms and the nonstoichiometric ratio of 1.23 has been detected.

In this work, the results of the computational experiments (CEs) of microheterogeneous combustion simulation in the "self-propagating high-temperature synthesis (SHS)" taking place in the Ti-Al layered structures (figure 1) have been analyzed. The SHS simulation in the nanoscale layered Ti-Al system is carried out by the "molecular dynamics (MD)" method realized in the LAMMPS package with capacity of parallel computing [1].

Figure 1. Structural description for two Ti-Al layered systems: (a) $N_{Ti}/N_{Al} = 1.15$, $N=936998$; (b) $N_{Ti}/N_{Al} = 1.23$, $N=453974$.

In both structures (figure 1), the each "big" layer contains the several atomic layers generating a crystal lattice of unit cells. The unit cells of Ti, having the hcp type, are characterized by the following parameters: $a = 0.29508$ nm, $c=0.46855$ nm [2]. The unit cells of Al, having the fcc type, are
characterized by the following parameter: \( a = 0.405 \) nm [3, 4]. The nonstoichiometric ratio of the first structure (figure 1(a)) is \( N_{\text{Ti}}/N_{\text{Al}} = 1.15 \). In other words, the Ti atom fraction make 53.5 % and the Al atom fraction make 46.5 %, respectively. The nonstoichiometric ratio of the second structure (figure 1(b)) is \( N_{\text{Ti}}/N_{\text{Al}} = 1.23 \). In other words, the Ti atom fraction make 55.2 % and the Al atom fraction make 44.8 %, respectively.

The primary temperature was make 800 K for the both Ti-Al structures (figure 1), and in this case the both systems were "relaxed" during of 0.4 ns under conditions of NPT-ensemble: a) the atom quantity in each of the both structures, respectively: \( N = 936998 \) and \( N = 453974 \); b) the external pressure \( P = 1 \) Bar; c) the temperature \( T = 800 \) K. At this stage of the simulation the periodic boundary conditions were established for all 3 dimensions.

In the next phase of molecular-dynamic simulation, the periodic boundary conditions for both Ti-Al structures are retained. In this phase of molecular-dynamic simulation, both structures ignite from 800 to 1400 K in the warm-up regions (50x1.4x27.5 nm and 50x1.4x13.5 nm, respectively) during of 0.1 ns subject to NVT-ensemble (V - the warm-up volume). In the next regions (for the both structures: 370x1.4x27.5 nm and 370x1.4x13.5 nm, respectively), the model of the NVE-ensemble (E - total atom energy) within 0.1 ns was used. In the next phase of molecular-dynamic simulation the study of SHS evolution (for the both Ti-Al structures) in the model of NVE-ensemble was executed. In addition, the "free" boundary conditions correspond to the boundaries of each studied structure along the X axis and along the Y and Z axes the periodic boundary conditions are retained.

The “embedded atom” model (EAM) of 2003 for the interatomic interaction potential [2] in CEs of molecular-dynamic simulation has been applied. Analyzing the "plateaus" of temperature profiles (figure 2), the combustion wave velocity (around 17 m/s) was evaluated. Nevertheless, the combustion wave velocity in the Ni-Al system under similar conditions was considerable greater (approximately 30 m/s) [5-8].

**Figure 2.** Set of dependencies of the combustion temperatures (temperature profiles) vs. the coordinate X in the consecutive moments of time: the heating from 800 to 1400 K in the warm-up region (50x1.4x27.5 nm) of the first structure; the nonstoichiometric ratio \( N_{\text{Ti}}/N_{\text{Al}} = 1.15 \); \( N = 936998 \).

Using the OVITO package [9] and the Ackland-Jones bond-angle method (as modifier in OVITO, [10]), designed to recognize and visualize the structures of unit (elementary) cells (fcc, bcc, hcp, ico and other) in a simulated atomic and molecular systems, an analysis was carried out of the amounts
and percentage of different types of unit cells in the structures of the samples in the consecutive moments of time of SH-synthesis (figures 3 and 4). Figures 3 and 4 have been applied for recognition of elementary cell types (figure 4) and combustion wave velocity estimation (approximately 17 m/s, obtained previously through the temperature profiles, figure 2). According to figure 2, the temperature of combustion is in the range of 1470-1490 K.

Figure 3. Set of the snapshots (microsections) of the distribution structure of Ti atoms (yellow dots) and Al atoms (blue dots) along the first structure in the consecutive moments of time: the homogeneous zones (on the left) correspond to the formation of intermetallic compounds; the nonstoichiometric ratio $N_{Ti}/N_{Al} = 1.15$; $N=936998$.

Figure 4. Set of the snapshots (microsections) of the types distribution structure of unit cells along the first structure (system) in the consecutive moments of time: hcp (Ti cells) – red dots, fcc (Al cells) – green dots, bcc – blue dots; the nonstoichiometric ratio $N_{Ti}/N_{Al} = 1.15$; $N=936998$.

The combustion temperature of 1470-1490 K (figure 2) is higher than the melting point of the Ti$_3$Al phase, so the TiAl$_3$ and TiAl phases can occur, except for the Ti$_3$Al phase. Body-centered tetragonal (bct) structure of the TiAl$_3$ phase is close to the bcc structure - blue dots dominate in the composition of lilac hue in figure 4.
Figure 5. Set of dependencies of the density (density profiles) vs. the coordinate X in the consecutive moments of time: the heating from 800 to 1400 K in the warm-up region (50x1.4x27.5 nm) of the first structure; the nonstoichiometric ratio $N_{Ti}/N_{Al} = 1.15; N=936998$.

The face-centered tetragonal (fct) structure of the TiAl phase is close to the fcc structure (green dots in the composition of lilac hue correspond to this phase). The density of the first structure (system) in the propagation zone of the combustion wave (profile of 16 ns on the figure 5) is about to 3.3 g/cm$^3$ and this value correspond to the TiAl$_3$ phase with the density range of 3.15-3.38 g/cm$^3$. The calculations results of the percentage of intermetallic compounds in the first system (first structure) using the OVITO package confirmed the increase of bcc structures and the decrease of hcp structures.

The results of CEs obtained for the second layered Ti-Al system ($N=453974$, nonstoichiometric ratio $N_{Ti}/N_{Al}=1.23$) are shown in figures 6 - 9. Analyzing the "plateaus" of temperature profiles (figure 6), the combustion wave velocity was evaluated. The front velocity is approximately constant and equal to 17 m/s in the time range of 0.5–8 ns. Then front velocity gradually increases to 22 m/s. According to figure 6, the temperature of combustion is in the range of 1470-1490 K (higher than the melting point of the Ti$_3$Al phase). In this way, in the second layered system ($N_{Ti}/N_{Al}=1.23; N = 453974$) the phases TiAl$_3$ and TiAl are also formed, but unlike the first case, the percentage ratio of the TiAl phase increases. In addition, a heterostructure appears in the time interval from 8 to 16 ns. According to the figures 8 and 9 (the cases corresponding to the 16 ns), three zones with sharp rectilinear boundaries are stand out (in them green dots are dominant in relation to a small number of blue dots). This dominance in these three zones indicate the dominance of the TiAl compound in relation to the TiAl$_3$ compound.

Elementary cells Al, having type fcc (correspond to green dots), in these three zones they cannot be as a phase of liquid Al, as in figure 8 there is no bright green hue in the corresponding zones. Therewith, the density value of 3.5 g/cm$^3$ (figure 9), corresponding to these three zones, is observed instead of a lower value of 2.3-2.4 g/cm$^3$, corresponding to the density value of liquid Al. The appearance of a heterostructure may be determined by the nonstoichiometric ratio of components of the initial Ti-Al system.
Figure 6. Set of dependencies of the combustion temperatures (temperature profiles) vs. the coordinate X in the consecutive moments of time: the heating from 800 to 1400 K in the warm-up region (50x1.4x13.5 nm) of the second structure; the nonstoichiometric ratio $N_{Ti}/N_{Al}=1.23$; $N=453974$.

Figure 7. Set of the snapshots (microsections) of the distribution structure of Ti atoms (yellow dots) and Al atoms (blue dots) along the second structure in the consecutive moments of time: the nonstoichiometric ratio $N_{Ti}/N_{Al}=1.23$; $N=453974$.

Figure 8. Set of the snapshots (microsections) of the types distribution structure of unit cells along the second structure (system) in the consecutive moments of time: hcp (Ti cells) – red dots, fcc – green dots, bcc – blue dots; the nonstoichiometric ratio $N_{Ti}/N_{Al}=1.23$; $N=453974$. 
Figure 9. Set of dependencies of the density (density profiles) vs. the coordinate $X$ in the consecutive moments of time: the heating from 800 to 1400 K in the warm-up region (50x1.4x13.5 nm) of the second structure; the nonstoichiometric ratio $N_{Ti}/N_{Al} = 1.23$; $N=453974$.

To determine the mechanism of the heterostructure emergence, it is necessary to carry out a cycle of additional computational experiments with varying different conditions for initiating SHS.

Computer molecular-dynamic simulation was carried out on the network cluster of 15 PCs (4-core Intel i5-7400 processors).

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