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Study of the rate thermokinetic characteristics of the synthesis of nickel and titanium aluminides in layered nanocomposite structures of thin films based on molecular dynamics simulation

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On the basis of molecular dynamics simulation, as the rate thermokinetic characteristics of the process of self-propagating high-temperature synthesis of nickel and titanium aluminides, the maximum temperature growth rate in the combustion front and the velocity of the combustion front in layered nanocomposite Ni/Al and Ti/Al thin films are studied. The maxima of the temperature growth rate in the combustion front and the velocity of the combustion front, calculated from thermograms in various cross sections of thin films under study with layer thicknesses from 1.3 to 8.13 nm, reach maximum values in the ranges of $10^{11}-10^{12}$ K/s and $17-50$ m/s, respectively. Linear dependences of the rate thermokinetic characteristics on the specific interface area of heterogeneous layers are established with the invariance of the stoichiometry and temperature of the sections of the stationary combustion regime.

Keywords: self-propagating high-temperature synthesis, thermokinetic characteristics, temperature growth rate, combustion wave front motion velocity, specific surface area, layered nanocomposite thin films, molecular dynamics simulation.

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Self-propagating high-temperature synthesis (SHS) is one of the promising techniques for production of nanoscale strengthening particles and thin films, which are suited for extreme operation conditions, from nanoscale initial reagents. Exothermic heat release in the SHS reaction ensures thermodynamic stability of the synthesized material; in addition, the high reaction rate of SHS helps constrain the growth and chemical degradation of thin films and strengthening particles. Intermetallic compounds based on nickel and titanium aluminides are regarded in metal physics and materials science as promising materials for high-tech applications in mechanical engineering (aircraft and rocket engineering and other fields). Such compounds have the following effective performance characteristics: relatively low density; high hardness; and heat, wear, and corrosion resistance.

Although it appears that many aspects of SHS of nickel and titanium aluminides have already been thoroughly examined experimentally, the specifics of microkinetics of SHS of these Intermetallic compounds in nanoparticles [1,2] and other layered and matrix nanocrystalline composite structures [3,4] remain understudied.

The present study makes use of the results of molecular dynamics simulation of SHS of nickel and titanium aluminides in layered nanocrystalline composite structures (Fig. 1, a), which was performed in LAMMPS [5]. These results were saved on an external drive as Res_i.dat files, where $i = 1, 2, \ldots, K$. File numbers i correspond to time points t_i in the „reference frame of the modeled SHS process“ with a pitch of 0.1 ns (end time t_K corresponds to the planned duration of the modeled SHS process, $t_K = 0.1K$ ns). Each Res_i.dat file is a record of output data on each of N atoms of the system in the following format: atom type (Ni, Ti, or Al); coordinates of an atom (x, y, z); velocities of an atom (v_x, v_y, v_z); forces acting on an atom (f_x, f_y, f_z); and kinetic energy E_a of an atom. Having divided the layered structure (Fig. 1, a) into thin domains (parallelepipeds) with a fine pitch (e.g., 4 nm along axis X aligned with long dimension $A = 420$ nm), we determined the total energy of all atoms in each domain (at each time point t_i). The „averaged“ temperatures of all domains at each time point t_i were then estimated based on the total energy of atoms in each domain and the Boltzmann constant. All domains had the same height H (along axis Z), which is equal to the sum of thicknesses of all five layers. The domain depth (along axis Y) was $B = 1.4$ nm. Three cross section of structures of both Ni–Al and Ti–Al systems (domains number 25, 50, and 75) with coordinates of 100, 200, and 300 nm along axis X were chosen for calculation of thermograms (Fig. 1, b). The maximum temperature growth rate $k_{T,\max} = (dT/dt)_{\max}$, which is proportional to the rate of exothermic heat release in the combustion front (SHS reaction rate), was determined by analyzing the linear sections of these thermograms.

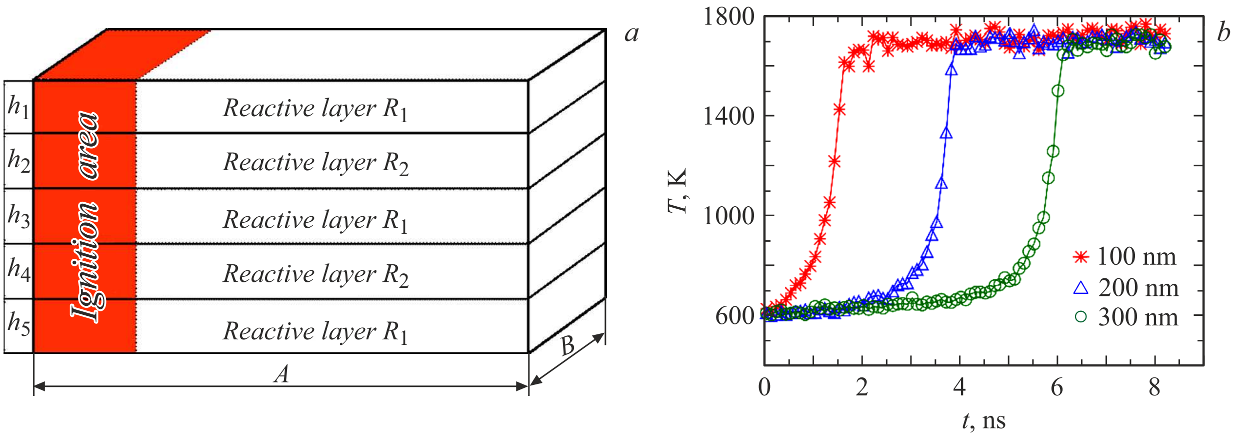

Figure 1. *a* — Image of layered nanocomposite structures for systems $R_1{-}R_2$ (R_1 is a layer of Ni atoms for the first Ni–Al system or a layer of Ti atoms for the second Ti–Al system and R_2 is a layer of Al atoms for both systems); *b* — typical thermograms in three cross sections for the first Ni–Al system containing 404 270 atoms.

Table 1. Parameters of layered nanocomposite Ni–Al structures and rate thermokinetic characteristics of SHS (at a stationary combustion temperature of 1690–1730 K)

Stoichiometry $N_{\mathrm{Ni}}/N_{\mathrm{Al}}$	Number of atoms in the system N_{total}	Layer thickness, nm				Specific surface area S_{SSA}, m^2/g	Temperature growth rate $k_{T,\max}\cdot 10^{-11}$, K/s	Ratio $\gamma = \frac{k_{T,\max}}{S_{\mathrm{SSA}}}\cdot 10^{-9}$, $\frac{\mathrm{K\cdot g}}{\mathrm{s\cdot m^2}}$	Velocity of the combustion front U_{front}, m/s
		h_1	$h_2 = h_4$	h_3	h_5				
1.275	946580	3.63	8.130	6.13	3.63	33.558	6.056	18.046	26.0
1.219	840346	3.00	7.500	5.50	3.00	39.073	7.477	19.136	28.9
1.228	741490	2.50	6.500	5.00	2.50	44.934	8.429	18.759	32.5
1.214	642736	2.35	5.600	4.00	2.35	51.648	9.901	19.170	35.8
1.217	587850	2.25	5.125	3.50	2.25	56.167	10.760	19.157	38.1
1.227	496520	1.77	4.380	3.38	1.77	64.933	12.199	18.787	43.1
1.221	404270	1.30	3.551	3.05	1.30	79.529	15.214	19.130	50.2

Figure 1, *b* presents three thermograms calculated for three cross sections of the Ni–Al layered system containing 404 270 atoms (N_{total}) with stoichiometric ratio $N_{\mathrm{Ni}}/N_{\mathrm{Al}} \approx 1.221$ (222 270 Ni atoms and 182 000 Al atoms). These three thermograms were analyzed to obtain two (similar) estimates of the „averaged“ velocity of the combustion front U_{front} (approximately 45 and 43.5 m/s) within the region of 100–300 nm along axis X. Thus, the combustion front velocity in macroscale powder mixtures, which does not exceed 10 cm/s, is almost 1000 times lower than the corresponding velocity in nanostructures.

Specific surface area S_{SSA} is expressed in $[\mathrm{m}^2/\mathrm{kg}]$ or $[\mathrm{m}^2/\mathrm{g}]$ and defined by ratio $S_{\mathrm{SSA}} = S/m$, where S is the interface area between the solid phase (in the present case, Ni or Ti layers) and the liquid Al layer and m is the mass of the solid phase. The interface area between the boundary (first and fifth) solid layers and liquid Al is $S_1 = S_5 = AB$, while both contacts with the Al layer need to be taken into account in calculations for the central (third) layer: $S_3 = 2AB$. Therefore, the total contact area between the solid phase layers (first, third, and fifth) and the liquid Al layers is $S_{total} = 4AB$, their overall thickness is $H_{solid} = h_1 + h_3 + h_5$, and their total volume is $V_{total} = ABH_{solid}$. The total mass of the solid phase is then $m_{total} = \rho_{solid}V_{total}$, and specific surface area S_{SSA} is given by

$$S_{\mathrm{SSA}} = S_{total}/m_{total} = 4/(\rho_{solid}H_{solid}), \qquad (1)$$

where ρ_{solid} is the density of the solid phase ($\rho_{\mathrm{Ni}} = 8.902\,\mathrm{g/cm^3}$, $\rho_{\mathrm{Ti}} = 4.51\,\mathrm{g/cm^3}$).

Since thickness values h_1 and h_5 are close and $h_3 \approx h_1 + h_5$, formula (1) takes the form $S_{\mathrm{SSA}} = 4/(\rho_{solid}H_{solid}) \approx 1/(\rho_{solid}h)$, where $h = (h_1 + h_5)/2$. Therefore, the specific surface area in thin films is governed largely by the minimum thickness of layers (or, in disperse systems, by dispersion degree of particles $1/h$, where h is the characteristic particle size). The results of calculation of the specific surface area and rate parameters of the SHS reaction for layered nanocomposite Ni–Al and Ti–Al structures are listed in Tables 1 and 2 and plotted in Figs. 2 and 3 (temperature fluctuations do not exceed 2–3%).

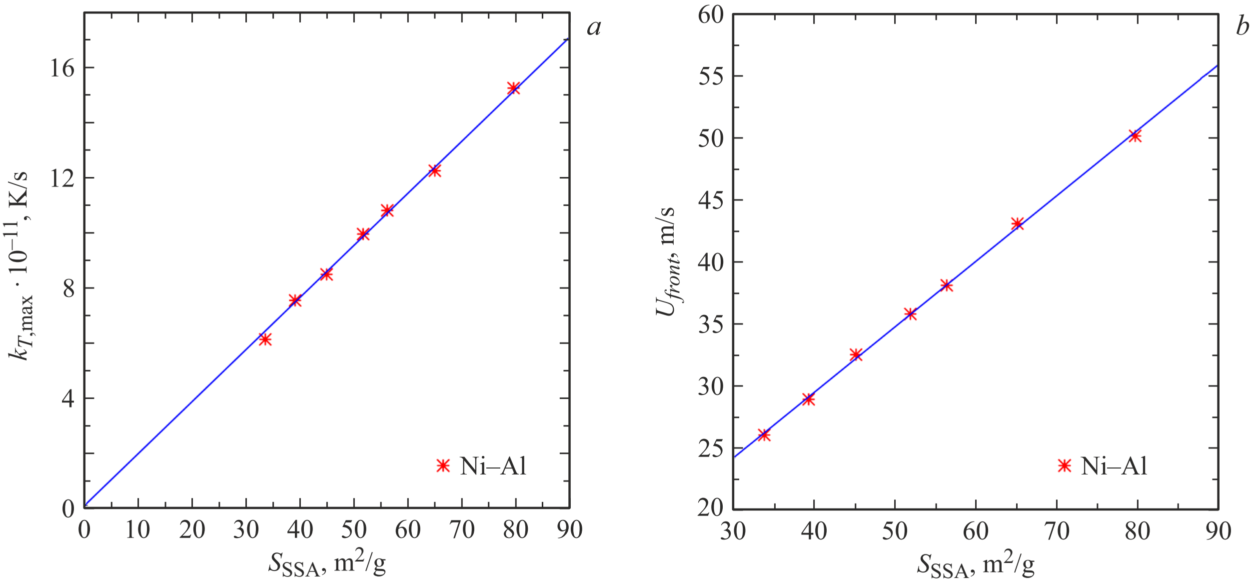

Figure 2. Dependences of the maximum temperature growth rate in the combustion front (*a*) and the velocity of the combustion front (*b*) on specific surface area S_{SSA} for the Ni–Al system.

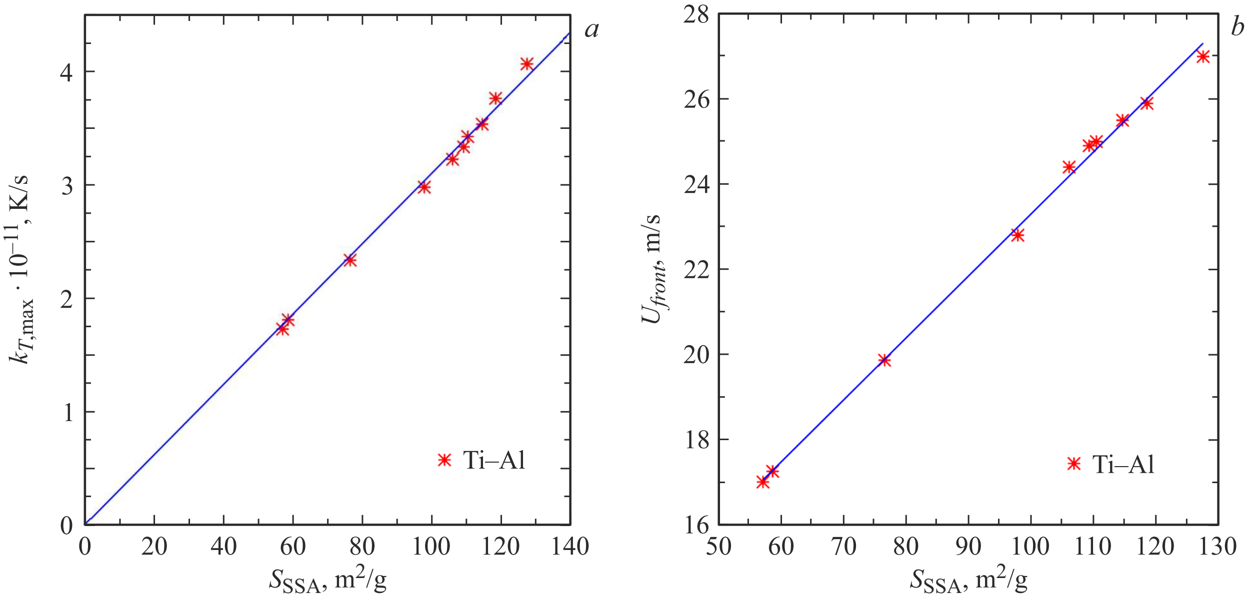

Figure 3. Dependences of the maximum temperature growth rate in the combustion front (*a*) and the velocity of the combustion front (*b*) on specific surface area S_{SSA} for the Ti–Al system.

In [6] (see Fig. 4), a temperature difference of 600 K for the linear combustion front section corresponds to a time on the order of 1.1 ns with complete melting of Ni and Al. The $k_{T,\max}$ estimate ($5.45 \cdot 10^{11}$ K/s) is fairly close to the data from Table 1.

The approximation of tabulated data was used to refine linear dependences

$$k_{T,\max} = \gamma \cdot 10^9 S_{\mathrm{SSA}}, \tag{2}$$

$$U_{front} = a + bS_{\mathrm{SSA}}. \tag{3}$$

For Ni–Al nanostructures:

$$1)\ \gamma = 18.977 \pm 0.113\ (0.596\%);$$
$$2)\ a = 8.4383 \pm 0.3803\ (4.507\%),$$
$$b = 0.52869 \pm 0.00694\ (1.313\%).$$

The deviations of stoichiometry from the mean value of 1.221 did not exceed 0.5%. At a stoichiometry value of 1.275 (Table 1), the deviation was 4.4%, and parameter γ was reduced accordingly by 4.9% to 18.046. For Ti–Al

Table 2. Parameters of layered nanocomposite Ti–Al structures and rate thermokinetic characteristics of SHS (at a stationary combustion temperature of 1460–1490 K)

Stoichiometry $N_{\mathrm{Ti}}/N_{\mathrm{Al}}$	Number of atoms in the system N_{total}	Layer thickness, nm				Specific surface area S_{SSA}, $\mathrm{m^2/g}$	Temperature growth rate $k_{T,\max}\cdot 10^{-11}$, K/s	Ratio $\gamma = \frac{k_{T,\max}}{S_{\mathrm{SSA}}}\cdot 10^{-9}$, $\frac{\mathrm{K\cdot g}}{\mathrm{s\cdot m^2}}$	Velocity of the combustion front U_{front}, m/s
		h_1	$h_2 = h_4$	h_3	h_5				
1.240	946682	3.965	6.000	7.80	3.80	56.982	1.725	3.027	17.00
1.150	936998	3.695	6.150	7.55	3.90	58.562	1.808	3.087	17.25
1.209	726024	3.100	4.600	5.40	3.10	76.458	2.331	3.049	19.86
1.242	530820	2.416	3.500	4.60	2.05	97.829	2.975	3.041	22.80
1.260	492707	1.817	3.175	4.55	2.00	106.002	3.219	3.037	24.40
1.215	485587	1.622	3.225	4.50	2.00	109.200	3.330	3.049	24.90
1.215	482740	2.135	3.100	4.00	1.90	110.382	3.421	3.099	25.00
1.182	475620	1.891	3.175	3.95	1.90	114.574	3.528	3.079	25.50
1.156	469923	2.085	3.250	3.45	1.95	118.493	3.758	3.171	25.90
1.045	445715	1.477	3.285	3.63	1.85	127.486	4.059	3.184	27.00

nanostructures:

$$1)\ \gamma = 3.0963 \pm 0.0191\ (0.617\%);$$

$$2)\ a = 8.7501 \pm 0.2574\ (2.942\%),$$

$$b = 0.14561 \pm 0.00256\ (1.76\%).$$

The deviations of stoichiometry from the mean value of 1.208 were 2–4%. At a stoichiometry value of 1.045 (Table 2), the deviation was 13.5%, and the parameter γ was increased accordingly by 2.84% to 3.184.

The SHS reaction rate (maximum temperature growth rate in the combustion front) increases with combustion temperature and specific interface area, but decreases with increasing concentration of the solid phase.

The known formula $S_{\mathrm{SSA}} = 6/(\rho d)$ was used to estimate the specific surface area ranges for powder Ni and Ti particles with size $d = 25{-}50\,\mu$m: 0.0135–0.027 and 0.027–0.54 $\mathrm{m^2/g}$, respectively. Relying on the determined values of parameter γ and formula (2), we then found predicted values of $k_{T,\max} = 2.55\cdot 10^8{-}5.1\cdot 10^8$ K/s for the Ni–Al system and $0.84\cdot 10^8{-}1.68\cdot 10^8$ K/s for Ti–Al. The results reported in [7] (see the dashed curve in Fig. 10) were used to obtain the following estimate of reaction time τ_r within composite Ni/Al particles 25–50 μm in size: 5–20 μs. Having divided the temperature difference (approximately 1000 K) accumulated in reaction time τ_r by time τ_r, we determined that $k_{T,\max}$ should fall within the range of $0.5\cdot 10^8{-}2\cdot 10^8$ K/s, which is close to the predicted range ($2.55\cdot 10^8{-}5.1\cdot 10^8$ K/s).

Thus, it was demonstrated that the rate thermokinetic characteristics of SHS in layered nanocomposites are three (or more) orders of magnitude higher than the corresponding parameters of SHS in powder mixtures.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S.O. Kart, H.H. Kart, T. Cagin, J. Nanoparticle Res., **22** (6), 140 (2020). DOI: 10.1007/s11051-020-04862-2

[2] V.I. Jordan, I.A. Shmakov, Commun. Comput. Inf. Sci., **1526**, 101 (2022). DOI: 10.1007/978-3-030-94141-3_9

[3] A.S. Rogachev, S.G. Vadchenko, F. Baras, O. Politano, S. Rouvimov, N.V. Sachkova, M.D. Grapes, T.P. Weihs, A.S. Mukasyan, Combust. Flame, **166**, 158 (2016). DOI: 10.1016/j.combustflame.2016.01.014

[4] V.I. Jordan, I.A. Shmakov, Commun. Comput. Inf. Sci., **1304**, 43 (2020). DOI: 10.1007/978-3-030-66895-2_4

[5] S. Plimpton, J. Comput. Phys., **117**, 1 (1995). DOI: 10.1006/jcph.1995.1039

[6] B. Witbeck, D.E. Spearot, J. Appl. Phys., **127** (12), 125111 (2020). DOI: 10.1063/5.0002036

[7] J.M. Pauls, C.E. Shuk, A.S. Rogachev, A.S. Mukasyan, Combust. Sci. Technol., **190** (5), 893 (2018). DOI: 10.1080/00102202.2017.1417269

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