

## **Regimes of synthesis in nanoscale multi-layer Ni/Al films on a substrate**

*O.S. Rabinovich<sup>1</sup>, P.S. Grinchuk<sup>1</sup>, M.A. Andreev<sup>2</sup>, B.B. Khina<sup>3</sup>*

*<sup>1</sup>A.V.Luikov Heat and Mass Transfer Institute, 15 P. Brovka Str, Minsk, 220072, BELARUS*

*<sup>2</sup>Institute of Powder Metallurgy, <sup>3</sup>Physico-Technical Institute*

### **Introduction**

Synthesis of nanoscale intermetallic, oxide and nitride films is a new technological method for production of coatings with unique properties for a variety of practical applications. The Ni-Al system is one of the most widely studied. Because of high melting temperature (1638 °C) of NiAl and its high chemical stability, the films of this material can be used as protective coatings for various machine components. A new and rapidly expanding area of research and development is the application of Self-Propagating High-Temperature Synthesis (SHS) in thin metal-metal films (including the Ni-Al system) for joining (soldering or welding) of temperature-sensitive and small-sized components [1,2]. Raw nano-scale layers have high reactivity due to a very short interdiffusion time. Because of this, carrying out the synthesis reaction in the regimes of combustion wave propagation or thermal explosion permits performing joining in a very short time ( $\sim 10^{-1}$ - $10^{-2}$  s) and with small specific heat release (heating of the system as a whole does not exceed 10-20 °C). The latter is especially important for joining of such temperature-sensitive materials as metallic glasses. Local heating during SHS in nanofilms also permits joining materials with substantially different coefficients of thermal expansion, for example a metal to ceramics.

Despite a large number of studies on the thermodynamics, kinetics and dynamics of SHS in Ni/Al nanofilms there are two problems related to this process which have not been solved in a sufficiently accurate way till now. The first problem is a detailed examination of the effect of heat losses into the substrate and the second one is a rigorous investigation of the growth of different phase layers taking into account both the diffusion processes and realistic phase diagram of the system. The latter problem is treated in full in a paper by B.B.Khina in these proceedings [3]. The former problem is analyzed in this work which is aimed at two-dimensional modeling of two conjugate processes: propagation of the synthesis wave in a multi-layer Ni/Al system and propagation of the thermal wave into substrate. The main question addressed in this work is the following: what are the conditions (first of all, the number of Ni/Al binary layers, initial temperature and heating rate) for the development of self-sustaining reaction towards complete formation of the final product.

### **Description of the theoretical model**

#### Main assumptions

In the present study, the theoretical model describing the synthesis of NiAl in a multi-layer nano-scale film deposited on a substrate is based on a number of main assumptions.

The first of them is that the film is isothermal in the transverse direction during the synthesis. This assumption follows from the comparison of a minimal reaction time in a binary Ni/Al layer,  $t_r$ , with the characteristic time of thermal relaxation  $t_{hr} \sim h^2/a_f$ , where  $h$  is the total thickness of the film and  $a_f$  is its thermal diffusivity coefficient. Since the estimate of the reaction time  $t_r$  is no less than  $10^{-4}$ - $10^{-5}$  s, the  $t_{hr}$  value remains much lower for the film thickness up to 10  $\mu\text{m}$ . For example, at  $a_f = 4.8 \cdot 10^{-5}$  m<sup>2</sup>/s and  $h = 10$   $\mu\text{m}$   $t_{hr}$  is equal to  $2 \cdot 10^{-6}$  s. We also assume that thermal contact between the film and the substrate is ideal, i.e. the temperatures and heat fluxes at the interface are equal.

The second assumption asserts that the growth of the product layer is determined by simplified diffusion kinetics (quasi-steady-state approximation). According to this model, the so-called parabolic kinetic law describes the macro-kinetic rate of the reaction between two neighboring layers of Ni and Al:

$$W(T, \eta) = \frac{k_0 \exp(-E/RT)}{\eta}, \quad (1)$$

where the conversion of reactants is determined as  $\eta = \frac{z}{\delta/2}$  (Fig. 1).

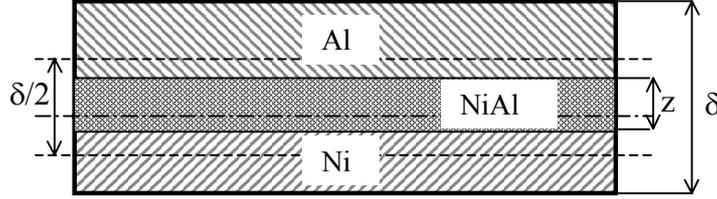


Figure 1. Simplified scheme of the product layer growth;  $z$  is the current thickness of product layer

According to the Eq. (1), the characteristic time of the reaction,  $t_r$ , is determined as the time of the product layer growth up to the value  $\delta/2$  due to interdiffusion of reactants through this layer:

$$t_r = [k_0 \exp(-E/RT)]^{-1} = \frac{\delta^2}{8D_0 \exp(-E/RT)} = \frac{\delta^2}{8D(T)}. \quad (2)$$

Here  $D(T)$  is the effective coefficient of interdiffusion of reactants through the product layer. Three different expressions for the interdiffusion coefficient in solid NiAl were used in the present modeling (Tab. 1).

Table 1  
Effective interdiffusion coefficient in NiAl

No.	$D_0, \text{m}^2/\text{s}$	$E, \text{kJ/mol}$	Ref.
1	$1.0 \cdot 10^{-4}$	221,96	[4]
2	$4,75 \cdot 10^{-8}$	115,9	[5]
3	$2,18 \cdot 10^{-6}$	137	[6]

When the temperature of the reactants reaches the melting point of NiAl, the interdiffusion coefficient undergoes a step-like change to its value in the melt and then varies as a linear function of temperature:  $D_m = D_{m0} T/T_m$ , where  $D_{m0} = 5,0 \cdot 10^{-9} \text{ m}^2/\text{s}$  [7],  $T_m = 1911 \text{ K}$ . It is also supposed that the thermophysical properties of the system are constant.

### Problem formulation

The geometry of the computational region and boundary conditions are presented in Fig. 2.

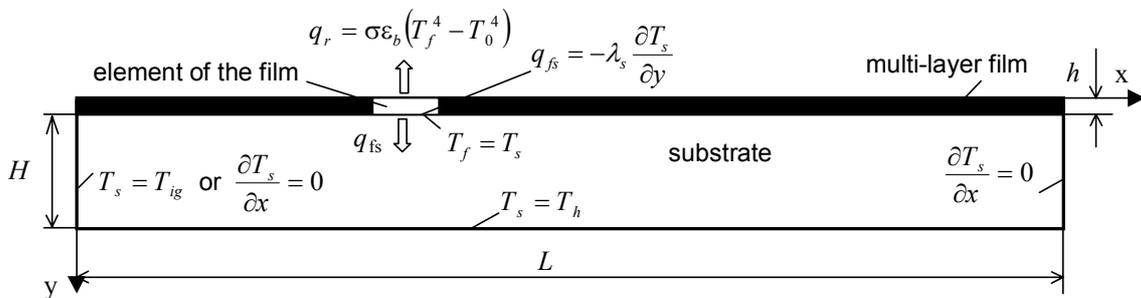


Figure 2. Sketch of computational region and boundary conditions for the energy transfer equations.

It is supposed that the substrate with the deposited film lies on a heater, and the system is placed in a vacuum chamber with temperature  $T_0$ .

The equation for the heat transfer in the film has the following form:

$$\frac{\partial T_f}{\partial t} = a_f \frac{\partial^2 T_f}{\partial x^2} - \frac{q_{fs} + q_r}{h \rho_f c_f} + \frac{Q}{c_f} W(T_f, \eta), \quad (3)$$

where  $q_{fs}$  and  $q_r$  denote the transversal heat fluxes from the film to the substrate and to the walls of the reaction chamber, correspondingly;  $Q$  is specific heat of the reaction (per unit mass);  $\rho_f$ ,  $a_f$  and  $c_f$  are the density, thermal diffusivity and specific heat capacity of the film.

Heat transfer in the substrate obeys the following two-dimensional heat-conductance equation:

$$\frac{\partial T_s}{\partial x} = a_s \left( \frac{\partial^2 T_s}{\partial x^2} + \frac{\partial^2 T_s}{\partial y^2} \right), \quad (4)$$

where  $a_s$  is the substrate thermal diffusivity.

In accordance with the above described diffusion-kinetic model of the product layer growth, an equation for the conversion degree can be written as follows:

$$\frac{d\eta}{dt} = W(T, \eta) = \frac{8D(T_f)}{\delta^2 \eta}, \quad \text{where } D(T_f) = \begin{cases} 0, & \text{at } T_f < T_{in} \\ D_0 \exp(-E/RT_f), & \text{at } T_{in} \leq T_f < T_m \\ D_{01} \frac{T_f}{T_m}, & \text{at } T_f \geq T_m \end{cases} \quad (5)$$

It is supposed that at the initial instant of the synthesis there is some amount of the product in the film, which was formed at the stage of film deposition. This product has a form of thin interlayers of thickness  $\delta_0$  located between the layers of reactive components. Thus, it can be said that the system is characterized by the initial conversion degree:

$$\eta|_{t=0} = \eta_0 = \frac{\delta_0}{\delta}. \quad (6)$$

The boundary conditions for the film and substrate are illustrated by Fig. 2. The radiant heat flux from the film surface to the camera walls is calculated by the Stephan-Boltzman law

$$q_r = \sigma \varepsilon_b (T_f^4 - T_0^4) \quad (6)$$

where the emissivity factor of the film  $\varepsilon_b$  varies from 0.8 to 1.0.

The heat flux from the film to the substrate is

$$q_{fs} = -\lambda_s \left. \frac{\partial T_s}{\partial y} \right|_{y=0}, \quad (7)$$

Two types of initial and boundary conditions were considered. In the first case, the initial temperature of the substrate and film are assumed to be equal to the heater temperature,  $T_h$ , which is hold constant, but the left boundaries of substrate and film have the temperature of igniter,  $T_{ig}$ .

$$T_{f,s}(x > 0, y) \Big|_{t=0} = T_h; \quad T_{f,s}(0, y) \Big|_{t \geq 0} = T_{ig} \quad (8)$$

The second type of initial (and boundary) conditions describes fast heating of the substrate and film by the heater to attain the thermal explosion regime. In this case, the initial temperature of the system as a whole was set equal to a sufficiently low initial temperature of the heater, and then the heater temperature was increased linearly with a given rate up to the prescribed final temperature. In both considered cases, the heat exchange between the substrate and the film is governed by Eq. (7).

### Dimensionless equations

Transition to the dimensionless form of above-obtained equations allows obtaining governing dimensionless parameters and gives certain advantages for numerical modeling of the process. The scales used for this purpose and characteristic dimensionless numbers are presented below.

For the stoichiometric mixture of Ni and Al it is natural to choose the melting temperature of the product (NiAl) as a characteristic temperature scale:  $T_* = T_m = 1911$  K.

Basing on this choice of characteristic temperature we arrive to the following scales and dimensionless parameters:

$\Delta T_* = RT_*^2/E$  is the characteristic temperature interval (here E is the activation energy in the temperature dependence of interdiffusion coefficient);

$\theta = \frac{T - T_*}{\Delta T_*}$  is the dimensionless temperature;

$t_* = t_r = \frac{\delta^2}{8D_0 \exp(-E/RT_*)}$  is the characteristic time of reaction;

$\tau = t/t_*$  is the dimensionless time;

$x_* = \sqrt{a_s t_*}$  is the characteristic width of reaction zone;

$\tilde{x} = x/x_*$ ;  $\tilde{y} = y/x_*$  are the dimensionless spatial coordinates;

$\beta = \Delta T_*/T_*$  is the temperature factor of the reaction rate;

$\frac{1}{\gamma} = \Delta T_{ad}/\Delta T_*$  is the dimensionless temperature rise in the film ( $\Delta T_{ad} = Q/c_f$ );

$a_{fs} = \frac{a_f}{a_s}$  is the relative coefficient of thermal diffusivity of the film;

$\chi_r = \frac{\sigma \varepsilon_b \Delta T_*^3 t_*}{h \rho_f c_f}$  is the dimensionless number characterizing radiant heat exchange between the film and the reactor walls;

$\chi = \frac{\lambda_s t_*}{h \rho_f c_f x_*} = \frac{x_* \rho_s c_s}{h \rho_f c_f}$  is the dimensionless number characterizing heat transfer from the film to the substrate;

$\theta_0 = -\frac{1}{\gamma}$ ,  $\theta_{ig} = \frac{T_{ig} - T_*}{\Delta T_*}$  are the dimensionless ambient and igniter temperatures, respectively.

After the transition to dimensionless form the master equations can be written as follows:

$$\frac{\partial \theta_f(\tau, \tilde{x})}{\partial \tau} = a_{fs} \frac{\partial^2 \theta_f}{\partial \tilde{x}^2} - \chi \tilde{q}_{fs} - \chi_r \tilde{q}_r + \frac{\Phi(\theta_f)}{\gamma \eta}, \quad (9)$$

$$\frac{\partial \theta_s(\tau, \tilde{x}, \tilde{y})}{\partial \tau} = \frac{\partial^2 \theta_s}{\partial \tilde{x}^2} + \frac{\partial^2 \theta_s}{\partial \tilde{y}^2}, \quad (10)$$

$$\frac{\partial \eta(\tau, \tilde{x})}{\partial \tau} = \frac{\Phi(\theta_f)}{\eta}, \quad (11)$$

where

$$\Phi(\theta_f) = \begin{cases} 0 & \text{at } \theta_f < \theta_{in} \\ \exp\left(\frac{\theta_f}{1 + \beta \theta_f}\right) & \text{at } \theta_{in} < \theta_f < \theta_m \\ \tilde{D}_{10}(1 + \beta \theta_f) & \text{at } \theta_f > \theta_m \end{cases}, \quad (12)$$

$$\tilde{D}_{10} = \frac{D_{10}}{D_0 \exp(-E/RT_*)}, \quad (13)$$

$$\tilde{q}_r = R(\theta_f, \theta_0)(\theta_f - \theta_0), \quad (14)$$

$$R(\theta_f, \theta_0) = \left(\theta_f + \theta_0 + \frac{2}{\beta}\right) \left[ \left(\theta_f + \frac{1}{\beta}\right)^2 + \left(\theta_0 + \frac{1}{\beta}\right)^2 \right]. \quad (15)$$

Boundary conditions to Eqs. (9),(10) are expressed below:

$$\tilde{y} = 0: \quad \theta_f = \theta_s; \quad \tilde{q}_{fs} = -\frac{\partial \theta_s}{\partial \tilde{y}},$$

$$\tilde{y} = \tilde{H} = \frac{H}{x_*}: \quad \theta_s = \theta_h(\tau), \quad (16)$$

$$\tilde{x} = 0: \quad \theta_s = \theta_{ig},$$

$$\tilde{x} = \tilde{L} = \frac{L}{x_*}: \quad \frac{\partial \theta_s}{\partial \tilde{y}} = 0.$$

Initial conditions for the case of forced reaction ignition by an igniter look as:

$$\tau = 0: \quad \eta(\tilde{x}, \tilde{y}) = \eta_0 = \frac{\delta_0}{\delta} \quad (17)$$

$$\theta_s(\tilde{x} > 0, \tilde{y}) = \theta_h; \quad \theta_s(\tilde{x} = 0, \tilde{y}) = \theta_{ig}$$

The system of Eqs. (9)-(17) was solved numerically by a finite difference method using a combined explicit-implicit scheme and the alternating direction method.

The physical properties of components of the modeled system, i.e. the reactants, product and substrate are presented in Tab. 2.

Table 2

Physical properties of the system components

Component		Ni	Al	NiAl	Glass (substrate)
Property					
Specific density, $\rho$ ,	kg/m <sup>3</sup>	8910	2700	5900	2500
Molar mass, $M$ ,	g/mol	58,7	27,0	85,7	--
Thermal conductivity, $\lambda$ ,	W/(m·K)	58,0	205,0	80,0	0.74
Heat capacity, $c$ ,	J/(kg·K)	439,0	903,0	588,0	880
Thermal diffusivity, $a$ ,	m <sup>2</sup> /s	1,483·10 <sup>-5</sup>	8,408·10 <sup>-5</sup>	4,850·10 <sup>-5</sup>	2,96·10 <sup>-7</sup>

It was also supposed that the temperature of reaction initiation was about 250-300 °C.

Modeling was performed for the above discussed three expressions for the effective coefficients of interdiffusion in the product taken from Refs. [4-6] (see Tab. 1). It should be noted that the choice of one or another of these coefficients leads not only to quantitative but also to qualitative differences in the dynamics of the synthesis process. In particular, for diffusion coefficient 1 and 3 from Tab. 1, the condition for stability of a 1D combustion wave,  $\alpha_{st} = 9.1\gamma - 2.5\beta > 1$  [8], is not satisfied ( $\alpha_{st}$  is equal 0.59 and 0.95, respectively), so the combustion process ought to be oscillatory. On the contrary, for diffusion coefficient 2 from Tab. 1,  $\alpha_{st} = 1.12$  and the combustion synthesis proceeds in a stable mode. The question about stability of the combustion synthesis mode for a real system is presently open and an answer can be found basing on experimental studies. The details related to a stable or oscillatory mode for modeled regimes is not discussed in the present paper.

### Conditions for different regimes of synthesis in multi-layer Ni/Al films

#### Analysis of dimensionless parameters

Synthesis in multi-layer nanofilms can be performed in three essentially different regimes (modes), i.e. (i) the regime of self-sustaining combustion propagation, or combustion wave, (ii) the thermal-explosion regime and (iii) the annealing regime. The first two regimes are characterized by a high temperature and high reaction rate, whereas the last regime is low-temperature and slow.

The regime of self-sustaining combustion wave is characterized by a high propagation velocity (from 1 to 30 m/s), and the temperature in the wave is close to the adiabatic one. Local ignition (fast heating of a small part of a sample) is needed to initiate this regime.

The regime of thermal explosion can be performed under sufficiently uniform and rapid heating of the film. In this regime, the temperature exhibits a very fast increase (at a rate of thousands K/s) almost simultaneously throughout the sample, which leads to rapid completion of the process. The heating that precedes the thermal explosion in the film should be sufficiently fast to exclude consumption of the components until the explosion starts. Thus, in practice one has to consider the thermal explosion with non-stationary boundary conditions.

In the third regime, when the self-accelerating reaction is impossible due to heat losses and slow heating of the sample, the annealing regime occurs. In this case, both the reaction rate and conversion

are virtually controlled by the temperature increase in the heater.

Analysis of the above-derived dimensionless parameters characterizing the system shows that the most important parameter which determines a boundary between the different synthesis regimes is  $\chi = (x_*/h)(\rho_s c_s / \rho_f c_f)$ . Indeed, parameter  $\chi_t$  describing the radiant heat losses is small and is not significant in high-rate processes. Parameter  $a_{fs}$ , the ratio of thermal diffusivities of the film and substrate, is fixed for given materials. Parameters  $\beta$ ,  $\gamma$  and  $\theta_{in}$  related to the kinetics of the reaction and accompanying heat release are also fixed. Finally, variation of the substrate thickness does not affect the process because it is much larger than the thickness of the thermally affected zone of the substrate, which is heated by the reacting film.

It is important that parameter  $\chi$  does not depend on the period  $\delta$  of a multi-layer structure but is determined by the value of interdiffusion coefficient at the characteristic temperature,  $T_*$ , the number of the layers in the film,  $N$ , and the ratio of thermal effectiveness of the substrate and film  $\rho_s c_s / \rho_f c_f$ .

This conclusion results from the definition of  $\chi$  after substituting the expression for  $x_*$  into the latter:

$$\chi = \frac{x_*}{h} \frac{\rho_s c_s}{\rho_f c_f} = \frac{\sqrt{a_s t_*}}{h} \frac{\rho_s c_s}{\rho_f c_f} = \frac{\sqrt{a_s \delta^2 / 8D_*}}{N \delta} \frac{\rho_s c_s}{\rho_f c_f} = \frac{\sqrt{a_s / 8D_*}}{N} \frac{\rho_s c_s}{\rho_f c_f}. \quad (18)$$

It is obvious that for synthesis in a self-sustaining mode parameter  $\chi$  should be sufficiently low either due to the high interdiffusion rate or a large number of binary layers in the film. The fact that this conditions are independent of  $\delta$  can be physically understood when taking into account that variation of  $\delta$  (for example, increasing) changes (increases) the specific heat release (per unit film length) and the time of the reaction in a similar way. So, the relation between heat release and heat losses for the considered part of the film remains unchanged under variation of  $\delta$ . Thus, the change of synthesis regimes in the film is determined mainly by the number of binary layers in the latter, at least until the film can be considered as isothermal in the transverse direction, i.e. for its width up to 10  $\mu\text{m}$ .

### Regime of combustion wave propagation

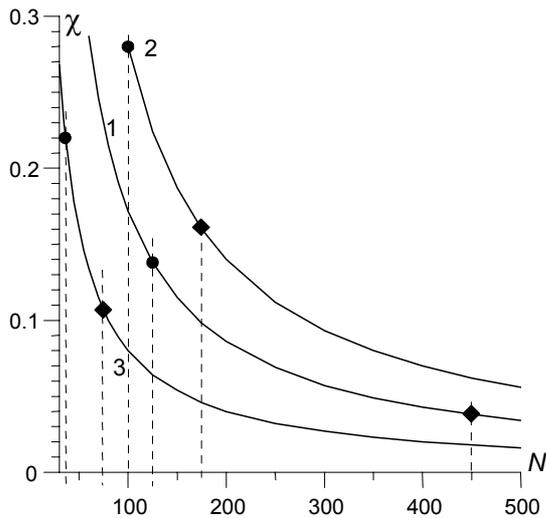


Figure 3. Parameter  $\chi$  vs. the amount of binary layers in a Ni/Al film on a glass substrate. Numbers at curves correspond to different values of the interdiffusion coefficient: 1, Ref.[4]; 2, Ref.[5]; 3, Ref.[6]. Rhombs denote the limits of SHS for initial temperature 300 °C and circles for 450 °C.

Numerical modeling has allowed calculation of critical values of parameter  $\chi$ , which determine the parametric boundary for synthesis in the combustion wave regime. In Fig. 3, these critical values are marked on the plots of parameter  $\chi$  as a function of  $N$ . Calculations were made for three aforesaid expressions for the effective interdiffusion coefficients for Ni/Al films deposited on the glass substrates having 0.2 mm in thickness. Figure 3 shows that the SHS wave can propagate in the considered system only at a sufficiently large number of binary layers. The data for critical numbers  $N$  are given in Table 2.

Table 2.

The numbers of binary Ni/Al layers providing SHS-mode on the glass substrate.

$T_h, ^\circ\text{C}$	Number of binary layers, $N$		
	$D_1$	$D_2$	$D_3$
300	450	175	73
450	125	100	36

It can be seen that a lower number of binary layers allowing synthesis in the SHS-mode corresponds to the 3<sup>rd</sup> expression for the diffusion coefficient. This expression was found in Ref. [6] by comparison of experimental data with numerical results obtained for the model much similar to the one proposed in this paper. Apparently, the results of our calculations with this diffusion coefficient can be considered as most close to the reality. However, final conclusion should be made after performing more detailed experiments.

Numerical modeling has also shown that propagation of an SHS wave in Ni/Al films deposited on metallic substrates is much more difficult in comparison with glass substrates. From the physical viewpoint it can be attributed to a considerable increase of heat transfer from the film to metallic substrate, which becomes apparent from the changes of parameters  $\chi$  and  $a_{fs}$ . For example,  $a_{fs}$  changes from 164 to 0.58 and parameter  $\chi$  changes from 0.080 to 132 when the glass substrate is replaced by aluminium one (for the diffusion coefficient  $D_2$ ). As a result of numerical modeling it is found that the number of binary layers needed for SHS-mode in the case of an aluminum substrate is 950 at  $T_h=300$  °C and 510 for  $T_h= 450$  °C.

#### Regime of thermal explosion

To carry out synthesis in the regime of thermal explosion it is necessary, along with having a large number of binary layers, to perform fast uniform heating of the film and substrate. The thermal explosion regime can be obtained only if at the instant of a sharp increase of the film temperature the initial reactants are not consumed substantially. Figures 4, 5 illustrate the dynamics of the film temperature and conversion for thermal explosion at different heating rates. Parameter  $\chi$  for the example presented in Fig. 4 is equal to 0.016 that corresponds to 500 binary layers at the diffusion coefficient  $D_3$  (most favorable conditions for the development of a self-sustaining reaction). As can be seen from the plots, a transition to the thermal explosion regime becomes distinct for a heating rate not less than 15 K/s. In films with relatively lower numbers of binary layers, the thermal explosion regime can be performed only at a high heating rate. Thus, for  $\chi=0.1$ , that corresponds to 75 binary layers for diffusion coefficient  $D_3$ , the thermal-explosion synthesis occurs at heating rates about 200 K/s (Fig. 5).

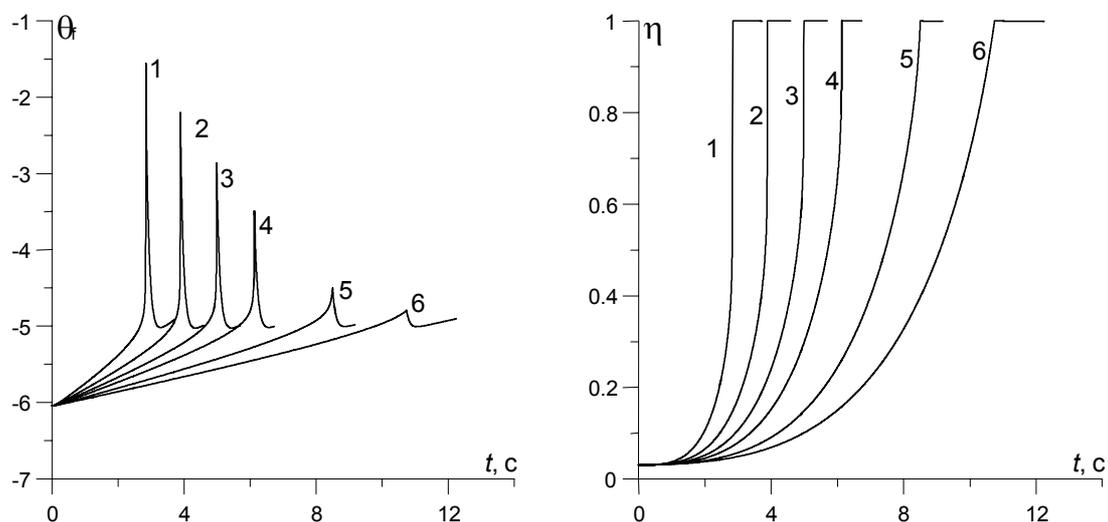


Figure 4. The film temperature vs. time for different heating rates in the thermal explosion regime for  $\chi=0.016$  (500 binary layers with the interdiffusion coefficient taken from Ref. [6]). The heating rates are 34 K/s (curve 1), 25.4 K/s (2), 20.4 K/s (3), 16.9 K/s (4), 12.79 K/s (5), 10.2 K/s (6).

The obtained results mean that it is impossible to realize the self-sustaining synthesis wave in a single binary layer of a film deposited on a substrate or to initiate a regime of thermal explosion in such films at heating rates below  $\approx 20$  K/s. This finding contradicts the interpretation given in works [9-11]. The

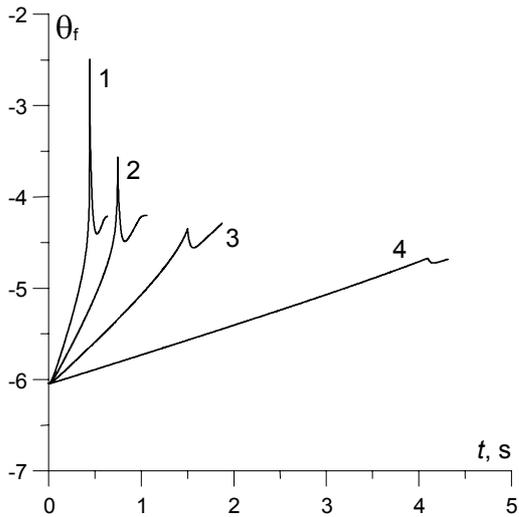


Figure 5. The film temperature vs. time for different heating rates in the thermal explosion regime for  $\chi=0.1$  (75 binary layers with the interdiffusion coefficient taken from Ref. [6]). The heating rates are 339 K/s (curve 1), 203 K/s (2), 102 K/s (3) and 33.9 K/s (4).

( $t_{heating} \sim h^2/a_f$ ) show that under these heating rates the film temperature follows the temperature of the substrate. The synthesis rate for this case is given by Eq. (5) where the temperature is a time-dependent function reflecting the substrate heating-up. In the present study, the linear heating functions were used. Heat transfer along the film is not important in the annealing regime, so it is possible to perform calculations of conversion in each point of the film independently. The dependencies of conversion degree on time and the film temperature found by the above described approach are presented in Fig. 6.

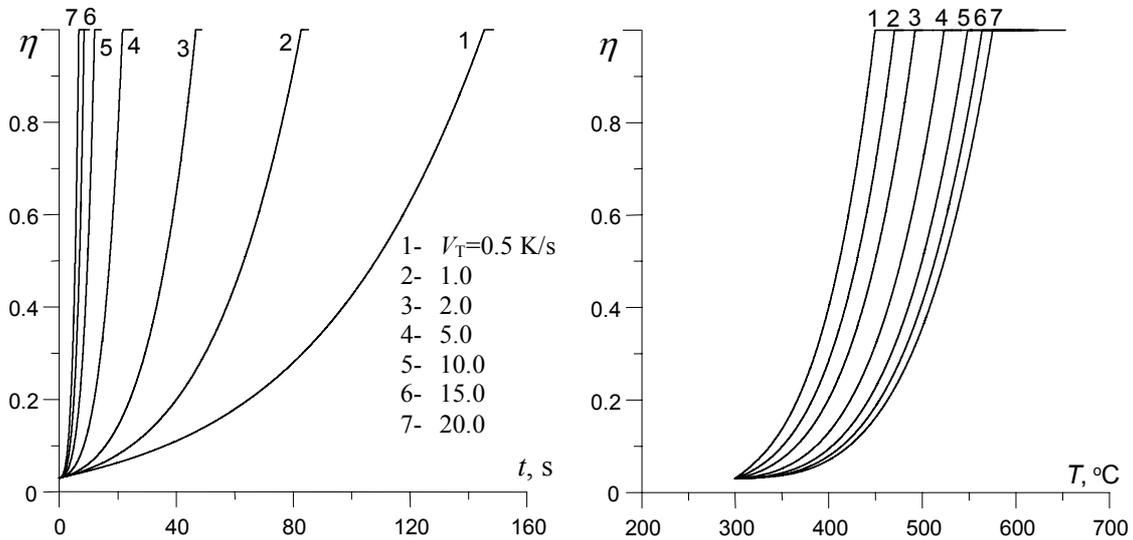


Figure 6. Conversion degree vs. time (a) and temperature of the substrate (b) at the number of binary layer  $N = 10$  ( $\chi=0.803$  at diffusion coefficient  $D_3$ ); the heating rates are shown in the figure; the initial time ( $t=0$ ) corresponds to the instant when the temperature becomes equal to that of reaction initiation  $T_{in} = 300$  °C.

Increasing the heating rate brings about a decrease in the synthesis time and a rise of the temperature that corresponds to completion of the synthesis (Fig. 7).

authors of these studies assert that they observed SHS-mode in two-layer films of Ni/Al, Al/Fe and Al/Co. Apparently, in these experiments, not an SHS wave was observed but just displacement of the reaction zone, which goes after the zone of non-uniform heating of a sample. This interpretation is supported by the values of the reaction zone displacement velocity found in the cited papers. This velocity was not higher than a few centimeters per second whereas the characteristic velocity of an SHS wave in multi-layer films should be, according to our calculations and experimental results by other authors, about tens meters per second.

#### Regime of annealing

At a small number of binary layers in a deposited film ( $N \sim 10$ ) and low heating rates ( $V_T \sim 1-50$  K/s), the synthesis can be performed only in the annealing regime. Estimations of the time of film heating-up

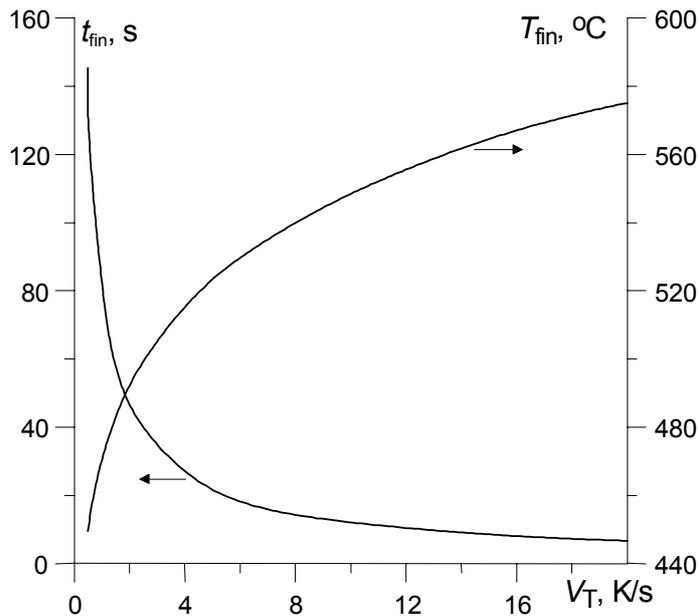


Figure 7. Time and the temperature of synthesis completion vs. the heating rate.  $N = 10$ ,  $\chi = 0.803$  (at diffusion coefficient  $D_3$ ); the initial time ( $t = 0$ ) corresponds to the instant when the temperature becomes equal to that of reaction initiation  $T_{in} = 300$  °C.

The calculated initial and final temperatures of synthesis in the annealing regime are in good agreement with the experimental data obtained in Ref. [9] on the synthesis in binary Ni/Al films at the heating rate about 20 K/s. The data on the velocity of the synthesis wave propagation from work [9] can also be successfully interpreted within the frame of the annealing regime theory when assuming non-uniformity of film heating. Thus, the synthesis wave velocities 0.5–1.0 cm/s reported in [9] correspond to the situation when the temperature at one of the edges of the film is by 20 °C higher than at the other edge. In our experiments on synthesis in multi-layer Ni/Al nanofilms deposited on glass and metallic substrates by the ion-beam method, the heating rate was approximately ten times lower and the observed synthesis wave velocity was correspondingly by the factor of ten lower, too.

### Conclusion

The proposed model of synthesis in multi-layer thin (nano-sized) films combines conjugate heat transfer in the film and substrate with a simple diffusion-type kinetics of the reaction between film components. The model permit predicting the conditions for performing synthesis in three different regimes, i.e. the SHS-regime, the thermal explosion regime and the annealing regime. It is shown that the regime of SHS wave can be performed only in films with sufficiently high number of binary layers regardless of the layer thickness. For the thermal explosion regime, high heating rates are needed (hundreds K/s for the films with a number of binary layers about 100). The annealing regime of synthesis has a number of distinctive features. One of the most important of them is a low temperature of the synthesis. This can be an essential advantage in such applications as welding of thermosensitive materials. Naturally, the time of synthesis in the annealing regime is much longer than in the self-accelerated regimes. Also, it should be taken into account that in the annealing regime the substrate is heated uniformly over all its width whereas SHS-regime leads to heating only a thin substrate layer adjacent to the film. But in the last case the temperature of heating is much higher.

The discussed distinctive features of different regimes of synthesis in multi-layer nanofilms on substrates should be taken into account when designing specific applications.

### Acknowledgements

The work was supported by The State Scientific Program "Nanomaterials and Nanotechnologies (NANOTECH 5.10)".

### References

- [1] Swiston AJ, Hufnagel TC, Weihs TP. (2003) *Acta Materialia* Vol. 48, pp. 1575-1580.
- [2] Wang J, Besnoin E, Knio OM, Weihs TP. (2004) *Acta Materialia* Vol. 52, pp. 5265-5274.
- [3] Khina BB. (2005) Modelling interaction kinetics during SHS in thin-film Ni-Al system: a diagram of phase formation mechanisms. This Conference.

- [4] Helander T, Agren J. (1998) *Acta Materialia* Vol. 47, pp. 1141-1152.
- [5] Wei H, Sun X, Zheng Q, Guan H, Hu Z. (2004) *Acta Materialia* Vol. 52, pp. 2645-2651.
- [6] Jayaraman S, et al (2001) *Combust. Flame* Vol. 124, pp.178-194.
- [7] Iida T, Guthrie RIL. (1988) *The Physical Properties of Liquid Metals*. Oxford: Clarendon Press.
- [8] Shkadinskii KG, Khaikin BI, Merzhanov AG. (1971) *Comb. Explos. Shock Waves* Vol. 7, No.1, pp. 15-22.
- [9] Miagkov VG, Zhigalov VS, Bykova LE, Maltsev VK. (1998) *Zhurnal Techn. Phys.* Vol. 68, No. 10, pp. 58-62 (in Russian).
- [10] Miagkov VG, Li LA, Bykova LE, Turpanov IA, Kim PD, Bondarenko GV, Bondarenko GN. (2000) *FTT (Physics of Solid State)* Vol. 42, No. 5, pp. 937-941 (in Russian).
- [11] Miagkov VG, Poliakova KP, Bondarenko GN, Poliakov VV. (2003) *FTT (Physics of Solid State)* Vol. 45, No. 1, pp. 131-133 (in Russian).