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# KINETICS MODELING IN THERMOCHEMICAL PRESSING OF POWDER INTERMETHETAL ALLOYS

*It was established that the activation energy for the reaction of the interaction of titanium and aluminum with the formation of intermetallics is 79 kJ/mol, which is ~ 1.8 times higher than the activation energy of Ni-Al alloys. It was established that intermetallic compounds in the Ti-Al system have high values of activation energy, and therefore, show the complexity of the course of the SHS reaction under normal conditions. To implement the thermal explosion regime, it is necessary to create the following conditions (б, $T_{am}$) in the furnace, under which the value of the Semenov criterion for this substance will be greater than the critical value $Se_{cr}$. To carry out the synthesis reaction with titanium aluminides, preheating is required. The calculation showed that to reach the synthesis temperature in the combustion mode in the Ti+Al system, preliminary heating of the system to ~ 100 °C (378 K) is sufficient.*

***Keywords**: modeling thermokinetic analysis, intermetallics, thermochemical reaction, thermochemical pressing, activation energy.*

*Встановлено, що для реакції взаємодії титану та алюмінію з утворенням інтерметалідів енергія активації становить 79 кДж/моль, що в ~ 1,8 раза вища за енергію активації Ni-Al сплавів. Встановлено, що інтерметалідні сполуки в системі Ti-Al мають високі значення енергії активації, а відтак, показують складність перебігу СВС-реакції в звичайних умовах. Для реалізації режиму теплового вибуху необхідно створити в печі такі умови (б, $T_{ср}$), за яких величина критерію Семенова для даної речовини буде більшою за критичне значення $Se_{кр}$. Для здійснення реакції синтезу алюмінідами титану необхідний попередній підігрів. Розрахунок показав, що для досягнення температури синтезу в режимі горіння в системі Ti+Al достатній попередній підігрів системи до ~ 100 °C (378 K).*

***Ключові слова**: моделювання, термокінетичний аналіз, інтерметаліди, термохімічні реакція, термохімічне пресування, енергія активації.*

## Problem's Formulation

The basis of self-propagating high-temperature synthesis is the use of heat, which is released during a strong exothermic reaction of the interaction of powder reagents [1]. One of the options for conducting SHS is heating at a given rate, which ends in a thermal explosion [2]. The main feature of this method of synthesis is that the initiation of the reaction is not carried out from the surface, but by heating the entire volume of the reactant. At the same time, depending on the ratio of the determining parameters, the maximum temperature can occur either in the center of the reaction volume or between the center and the surface.

## Analysis of recent research and publications

The thermodynamic admissibility of the SHS process is a necessary, but not yet sufficient, condition for its implementation [3, 4]. In real conditions, when the heat losses are not equal to zero, for the stationary propagation of the combustion wave, it is necessary that the reaction rate and, therefore, the rate of heat release in the reaction zone, be much higher than the rate of heat transfer to the environment. In addition, the reaction rate should increase rapidly with increasing temperature (at

the initial temperature, no interaction should occur) [5]. It is customary to write the temperature dependence of the rate of a chemical reaction in the form [6]:

$$U = \sigma_n a \frac{c}{Q} \frac{RT^2}{E} k \exp\left(-\frac{E}{RT}\right), \quad (1)$$

where $E$ — activation energy of this reaction; $y_n$ — a constant that depends on the order of the reaction (for example: for $n = 0$, $y_n = 2$; for $n = 1$, $y_n = 1{,}1$; for $n = 2$, $y_n = 0{,}73$); $a$ — thermal conductivity;

$k$ — includes a weak, compared to exponential, static dependence on temperature.

Substituting this expression into the formula of Y.B. Zeldovich, for the burning rate in the approximation of narrow reaction zones we obtain [6]:

$$\Phi(T) = k(1-\eta)^n \exp\left(-\frac{E}{RT}\right). \quad (2)$$

This equation can be used to estimate the effective or apparent activation energy of a combustion reaction. To do this, it is necessary to build an experimental dependence of the formation of intermetallics on temperature.

The foundations of the theory of thermal explosion were developed by N. N. Semenov, who considered the equation of the heat balance of the reacting substance under the assumption of the uniformity of the temperature distribution over its volume. A chemical reaction is considered a zero-order reaction, when the reaction rate does not depend on the degree of transformation of the substance, but depends only on the temperature (according to the Arrhenius law). Then the rate of heat transfer from the chemical reaction in the substance will be determined by the expression [7]:

$$Q_{c\sim} = \dot{Q}cVk_0 e^{-\frac{E}{RT}} = QcVk_0 exp\left(-\frac{E}{RT}\right), \quad (3)$$

where $Q$ — thermal effect of the reaction, J/kg; $c$ — substance density, kg/m$^3$; $V$ — volume of substance, m$^3$; $k_0$ — pre-exponential factor, 1/s; $E$ — activation energy, J/mol; $R$ — universal gas constant, which is equal to 8.31 J/(mol·K).

The rate of heat removal from the substance to the environment is determined by Newton's law:

$$Q_{rem} = бS(T - T_{am}), \quad (4)$$

where $б$ − heat transfer coefficient, W/(m$^2$·K); $S$ − surface area of the substance, m$^2$.

Semenov N. N. showed that in terms of heat, two modes of reaction are possible: stationary and thermal explosion.

In the stationary mode $Q_{cr} = Q_{rem}$, thermal equilibrium is carried out: as much heat is released in the substance, as much of it is released into the environment. The temperatures reached in this mode are low, close to the ambient temperature $T_{am}$. They are derived from the equilibrium equation:

$$QcVk_0 exp\left(-\frac{E}{RT}\right) = бS(T - T_{am}). \quad (5)$$

The steady-state mode is established in the case of low ambient temperature $T_{am}$ values and sufficiently strong heat dissipation into the environment.

In the case of high values of the medium temperature and weak heat dissipation, the equilibrium equation no longer has a solution, since here $Q_{cr} > Q_{rem}$ at any temperature $T > T_{am}$. As a result of the exponential dependence of the rate of heat release on the temperature, self-heating of the substance occurs with a sharp, progressive self-acceleration, and at the same time very high temperatures are reached [7, 8].

Semenov N. N. found critical conditions separating the region of stationary regimes from the region of thermal explosion. They are determined by the critical value of the dimensionless Semenov criterion [9]:

$$Se = \frac{QcV}{бS} \frac{E}{RT_{am}^2} exp\left(-\frac{E}{RT_{am}}\right), \quad (6)$$

$$Se_{cr} = \frac{1}{e} = 0.368.$$

When $Se < Se_{cr}$ the process proceeds without an explosion, when $Se > Se_{cr}$ a thermal explosion occurs. Knowing the kinetic and thermophysical properties of the reactant substance ($Q$, $k_0$, $E$, $c$, $c$), its shape and dimensions ($V$, $S$), as well as the conditions in which it exists ($б$, $T_{am}$), you can easily calculate the value of the Semenov criterion $Se$.

To implement the regime of thermal explosion of a substance, it is necessary to create such conditions in the furnace ($б$, $T_{am}$), in which the value of the Semenov criterion for this substance will be greater than the critical value $Se_{cr}$. As can be seen from formula (6) for this criterion, its value is greater, the larger the values of $Q$, $c$, $V$, $k_0$, $T_{am}$ and the smaller the values of $б$, $S$. Therefore, determining the activation energy of intermetallic systems *Ni-Al* and *Ti-Al* will allow to calculate the critical conditions and period of induction of these reactions.

**Formulation of the study purpose**

The purpose of the work is to establish the kinetic regularities of the mechanism of chemical reactions of the formation of *Ni-Al* and *Ti-Al* intermetallic alloys and to determine their activation energy.

**Presenting main material**

To study the processes of interaction of nickel and aluminum in the solid state, the samples were annealed at temperatures from 300 to 500 °C every 10 °C with different exposure times (~ 5 min). In the *Ni-Al* system, a clear latent period is observed, the duration of which decreases with increasing temperature. After studying the structure of *Ni-Al* samples depending on the temperature and heating time, it was possible to record the moment of appearance of intermetallics of a certain size (0.5...1.0 мм) at each of the investigated temperatures. The obtained set of empirical values was approximated by the method of least squares according to the exponential equation [10, 11]. With the help of the package of applied programs for engineering and mathematical calculations SciLab, the calculated values of the activation energy and the pre-exponential index were found, and the equation is presented in the form of a graph of temperature-time dependence (Fig. 1).

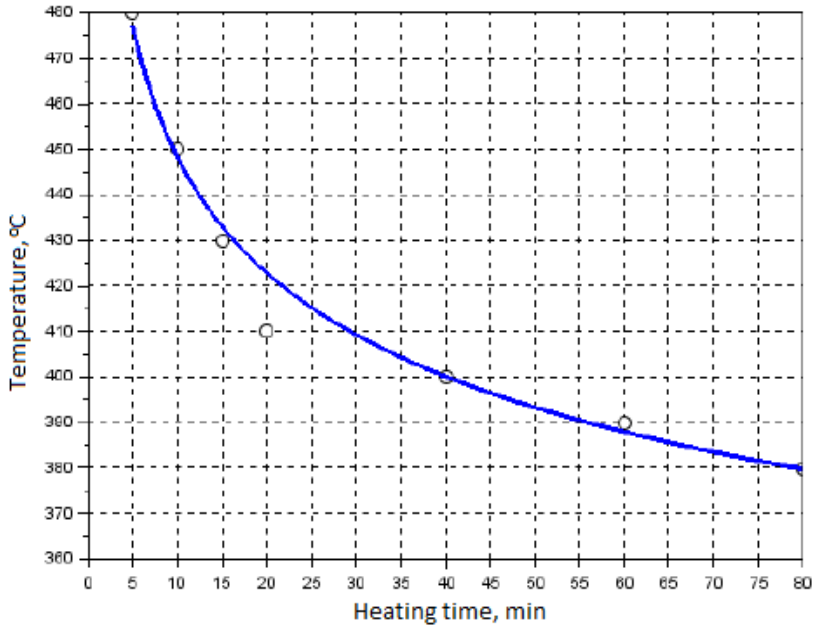


*Fig. 1.* Temperature-time dependence of the formation of intermetallics in the Ni-Al system

The computational and analytical dependence of the formation of the first intermetallics in the Ni-Al system is presented in the form of an equation [12]:

$$\tau = 1{,}0 \cdot 10^{-4} \exp\left(\frac{42917}{RT}\right), \tag{7}$$

which makes it possible to determine the rate of formation of the first sections of the intermetallic phase [12]:

$$\dot{N} = 5{,}76 \cdot 10^{6} \exp\left(\frac{-42917}{RT}\right). \quad (8)$$

Therefore, according to experimental results, the activation energy of the formation of the first intermetallic crystals is approximately 43 kJ/mol.

Conducted studies on heating samples of compounds and subsequent metallographic studies showed that at each temperature there is a latent period during which intermetallics are not detected in the contact zone. For the Ti-Al system, it was possible to detect the formation of intermetallics at a temperature of 510 °C only after 80 minutes of isothermal annealing. The temperature-time dependence of the appearance of intermetallics in the *Ti-Al* system is presented in Fig. 2. The initial stage of structure formation of titanium aluminides is the melting of aluminum, caused by a thermal pulse, and its subsequent spreading in the channels of the capillary-porous medium [10, 13]. Further diffusion of aluminum atoms into the lattice of titanium particles leads to the nucleation of the first crystals of the $TiAl_3$ intermetallic phase in the diffusion zone.

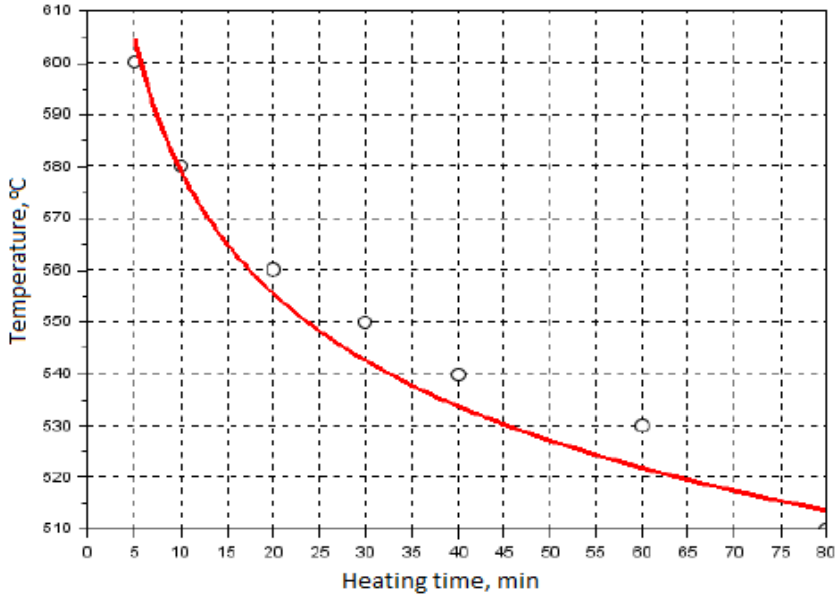


*Fig. 2*. Temperature-time dependence of the formation of intermetallics in the Ti-Al system

Calculation of the temperature-time dependence of the formation of the first intermetallics in the Ti-Al system allows us to determine the equation [13]:

$$\tau = 8{,}0 \cdot 10^{-7} \exp\left(\frac{78676}{RT}\right), \quad (9)$$

which makes it possible to determine the activation energy of the formation of the first intermetallic crystals in the Ti-Al system ~ 79 kJ/mol.

Accordingly, the rate of formation of the first intermetallics at the interface between titanium and aluminum is [13]:

$$\dot{N} = 7{,}2 \cdot 10^{8} \exp\left(\frac{-78676}{RT}\right). \quad (10)$$

Analytical equations of the temperature-time dependences of the formation of intermetallics in the *Ni-Al* and *Ti-Al* systems and their activation energies were obtained on the basis of experimental methods of studying the kinetics of the interaction of intermetallic alloys under the conditions of SHS. It was established that for the reaction of the interaction of nickel and aluminum with the formation of the first intermetallic crystals, the activation energy is 43 kJ/mol, which is ~ 1.8 times lower than the activation energy of *Ti-Al* alloys. Intermetallic compounds in the *Ti-Al* system have high values of

activation energy, and therefore show the complexity of the course of the SHS reaction under normal conditions. To carry out the synthesis reaction in the *Ti-Al* system, it is necessary to preheat the system to a temperature of 400...600 K.

Therefore, two methods of determining the activation energy of the intermetallic formation reaction are considered: a theoretical calculation method based on the results of thermodynamic analysis of the course of thermochemical reactions, and an experimental method based on the study of the kinetics of the formation of intermetallic phases. It was established that the difference between the values of activation energies obtained by two different methods does not exceed 5 % (Tabl. 1).

*Table 1.* Comparative analysis of calculations of activation energies obtained by two methods

| Activation energy, kJ/mol | Method | | Relative error, % |
|---|---|---|---|
| | Theoretical analysis | Experimental studies | |
| *NiAl* | 45,153 | 42,917 | 4,95 |
| *TiAl* | 82,263 | 78,676 | 4,36 |

The comparative analysis showed the reliability of the obtained values, which can be used for further calculations of the physicochemical model of the course of reactions in intermetallic systems under non-stationary temperature conditions.

For the numerical solution of the thermal problem of the synthesis of titanium and nickel aluminide under the conditions of SHS, the following initial data were integrated into the thermal model of Semenov:

– *Ni-Al* system: $Q_{NiAl} = 1{,}2 \cdot 10^3$ J/kg, $c_{NiAl} = 5870$ kg/m$^3$, $V = 30 \cdot 10^{-3}$ m$^3$, б $_{NiAl} = 400$ Wt/(m$^2$·K), $S = 33{,}4 \cdot 10^{-4}$ m$^2$, $E_{NiAl} = 42917$ J/mol, $k_0 = 5{,}76 \cdot 10^6$ 1/s.

– *Ti-Al* system: $Q_{TiAl} = 8{,}1 \cdot 10^3$ J/kg, $c_{TiAl} = 3800$ kg/m$^3$, $V = 30 \cdot 10^{-3}$ m$^3$, б $_{TiAl} = 240$ Wt/(m$^2$·K), $S = 33{,}4 \cdot 10^{-4}$ m$^2$, $E_{TiAl} = 78676$ J/mol, $k_0 = 7{,}2 \cdot 10^8$ 1/s.

Graphical interpretation of the obtained calculation results is presented in Fig. 3 and Fig. 4.

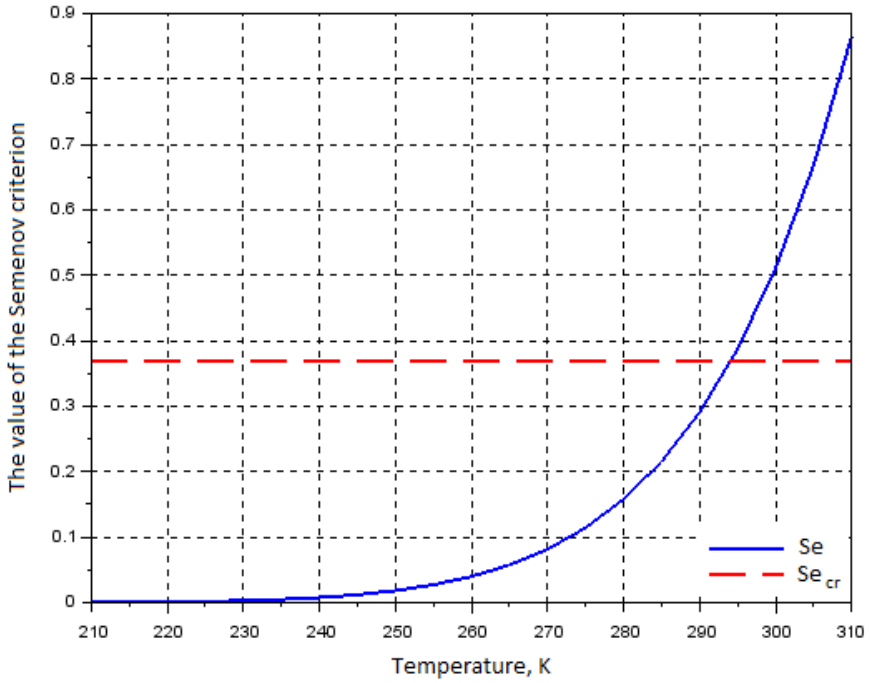


*Fig. 3.* Dependence of Semenov's calculation criterion on the initial synthesis temperature of the *Ni-Al* intermetallic systems

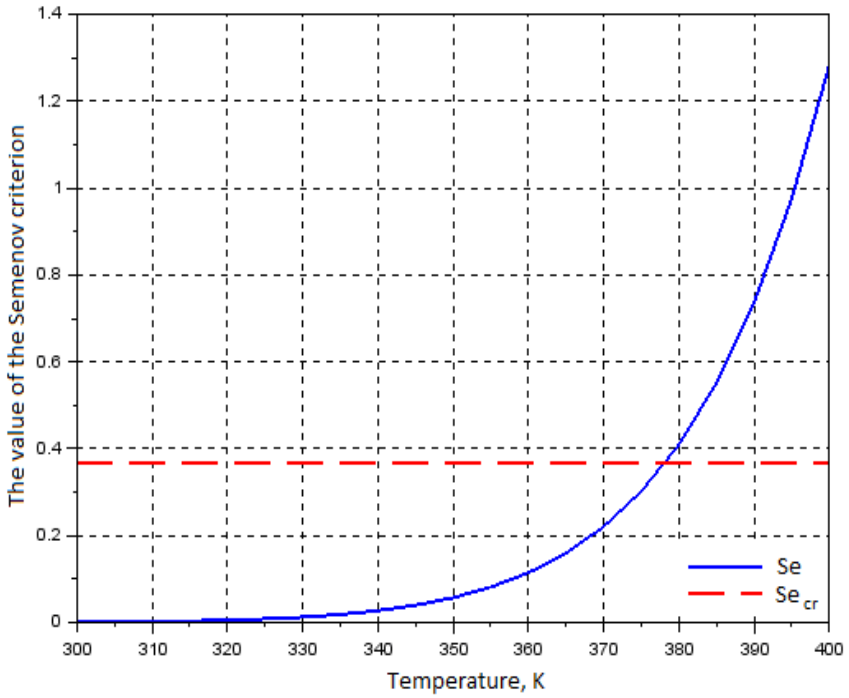


*Fig. 4.* Dependence of Semenov's calculation criterion on the initial synthesis temperature of the *Ti-Al* intermetallic systems

## Conclusions

Analysis of the calculation results showed that for the *Ni-Al* intermetallic system, the calculated value of the Semenov criterion is higher than the critical value. This condition is sufficient for self-propagating high-temperature synthesis to occur in the system under normal conditions.

The temperature analysis of the SHS reactions of the formation of intermetallics based on the ratio of the calculated Semenov criterion and its critical value showed that the studied reactions can be divided into two groups. The first group includes systems in which Semenov's calculation criterion is lower than its critical value ($Se < Se_{cr}$). First of all, this is the *Ti + Al* system, in which the occurrence of SHS under normal conditions ($T_0$ = 298 K) is unlikely. To carry out the synthesis reaction, preliminary heating is necessary. The calculation showed that to reach the synthesis temperature in the combustion mode in the *Ti + Al* system, heating up to ~ 100 °C (378 K) is sufficient. The second group includes systems for which the Semenov calculation criterion is equal to or exceeds the critical value ($Se > Se_{cr}$). This group includes the *Ni + Al* system, which, as shown by the temperature calculation of the Semenov criterion, is characterized by interaction in the combustion mode under normal conditions.

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## МОДЕЛЮВАННЯ КІНЕТИКИ ПРИ ТЕРМОХІМІЧНОМУ ПРЕСУВАННІ ПОРОШКОВИХ ІНТЕРМЕТАЛІДНИХ СПЛАВІВ

**Середа Б.П., Бєлоконь Ю.О., Кругляк І.В., Середа Д.Б., Кругляк Д.О.**

**Реферат**

Встановлено, що для реакції взаємодії титану та алюмінію з утворенням інтерметалідів енергія активації становить 79 кДж/моль, що в ~ 1,8 раза вища за енергію активації Ni-Al сплавів. Встановлено, що інтерметалідні сполуки в системі Ti-Al мають високі значення енергії активації, а відтак, показують складність перебігу СВС-реакції в звичайних умовах. Для реалізації режиму теплового вибуху необхідно створити в печі такі умови (б, $T_{ср}$), за яких величина критерію Семенова для даної речовини буде більшою за критичне значення $Se_{кр}$. Для здійснення реакції синтезу алюмінідами титану необхідний попередній підігрів. Розрахунок показав, що для досягнення температури синтезу в режимі горіння в системі Ti+Al достатній попередній підігрів системи до ~ 100 °C (378 K).

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