1. PHYSICO-CHEMICAL BASIS OF THERMOCHEMICAL PRESSING

According to the thermodynamic assessment of predicting the possibility of the course of the thermochemical process [1, 2], all investigated reactions of the formation of chemical compounds were divided into two groups based on the ratio of the adiabatic combustion temperature and the melting temperature of the product formed. In the first group, a system is selected in which the adiabatic combustion temperature is lower than the melting temperature of the resulting compound, the *Ti-Al* system is selected ($T_{ad} < T_{melt}$). From the second group, a system was selected for which the adiabatic combustion temperature is equal to or exceeds the melting temperature of the product formed – the *Ni-Al* system ($T_{ad} \geq T_{melt}$). Therefore, the object of the study was *Ni-Al* and *Ti-Al* intermetallic alloys, which belong to two different systems.

1.1. Thermodynamic analysis of thermochemical reactions

1.1.1. Calculation of adiabatic temperatures of intermetallic formation reactions

When evaluating the possibilities of obtaining various inorganic compounds, in particular aluminides, by the method of thermochemical pressing, thermodynamic analysis, primarily the determination of the maximum adiabatic temperatures of the process, is of significant importance. A significant amount of data on the thermodynamic analysis of the reactions of the formation of carbides, borides, nitrides and other compounds has been published. However, there is absolutely no such information about intermetallics. This is due to the lack of data on their thermodynamic properties, such as heat capacity and entropy, in the reference literature. At the same time, various empirical and semi-empirical methods of estimating the listed values are known.

Therefore, it is of indisputable interest to conduct a thermodynamic analysis of the reactions of intermetallics formation using such methods that allow estimating unknown quantities with a sufficient level of accuracy. The most reliable way to predict the possibility of a thermochemical reaction in any mixture is to calculate the adiabatic combustion temperature of this mixture. This temperature must be high enough to ensure an intense heterogeneous reaction. It is desirable that the adiabatic combustion temperature is higher than the melting point of at least one of the components. So, let's briefly consider the methodology and results of calculating the combustion temperature.

Temperatures of thermochemical processes are usually calculated under the assumption of adiabaticity, i.e. absence of heat loss from the reaction zone, in case of complete conversion of reactants into final products. At the same time, the equality of the enthalpies of the initial substances at the initial temperature T_o and of the final products at T_{ad} [1, 2] must be fulfilled:

$$\sum_{i=1}^{n}\left[H\left(T_{ad}\right)-H\left(T_{o}\right)\right]_{i}=\Delta H=Q_{x}, \tag{1.1}$$

where T_o – adiabatic and initial reaction temperatures, K;

Q_x − thermal effect of the reaction, kJ/mol. Data are summarized for all reaction products.

If one product is formed, equation (1.1) takes the form:

$$\int_{T_o}^{T_{ad}} C_p\left(T\right)dT=Q-\mu\cdot L, \tag{1.2}$$

where $C_p(T)$ − heat capacity of the reaction product, J/kg · K;

Q, L – the heat of formation and melting of the product, respectively, kJ/mol;

μ – the proportion of the liquid phase in the combustion product;

$$\mu=\begin{cases}0 & when\,T_{ad}<T_{melt}\\ 1 & when\,T_{ad}>T_{melt}\end{cases}. \tag{1.3}$$

If $T_{ad} = T_{melt}$ then $0 < \mu < 1$. The portion of the high-temperature phase for the $T_{ad} = T_{melt}$ case can be determined by the formula:

$$\mu = \frac{Q - \bar{c}\left(T_{melt} - T_0\right)}{L}, \tag{1.4}$$

where $\bar{c}$ – the heat capacity of the reaction products, averaged over the temperature range $T_0 = T_{ad}$, J/kg · K.

In the simplest case, one product of the reaction formed from the elements:

$$\sum_{i=1}^{n} X_i \to Z. \tag{1.5}$$

Then equation (1.1) can be transformed into equation (1.2). Usually, the value of T_{ad} is found from the solution of equation (1.2). Using the expression for the average heat capacity and the thermal effect of the process:

$$\bar{c} = \frac{1}{T_{ad} - T_0} \int_{T_0}^{T_{ad}} c\left(T\right) dT; \tag{1.6}$$

$$\bar{Q} = Q - \mu \cdot L; \tag{1.7}$$

(1.2) can be rewritten for greater clarity in the form:

$$T_{ad} \approx T_0 + \frac{\bar{Q}}{\bar{c}}. \tag{1.8}$$

In some works a more general approach was used, which considers chemical and phase equilibrium in multicomponent combustion products and allows calculating not only the combustion temperature, but also the composition of the products [1, 3]. For gasless combustion of a single-phase product, both approaches give the same result.

Therefore, to calculate the adiabatic combustion temperature, it is necessary to know the standard values of the heat of formation of ΔH_{298} compounds, the temperature dependence of their heat capacity $C_p(T)$, and the heat of fusion L.

The biggest difficulties in thermodynamic analysis arise as a result of the lack of the formed compounds' temperature dependence of the heat capacity. The heat of formation of a significant number of these compounds is given in the reference literature [4, 5]. Approximate semi-empirical methods are used to obtain equations for determining heat capacity and heat of fusion. There are several methods for calculating the heat capacity of compounds, for example, Neumann – Kopp, Landia, and others. The calculation of the heat capacity, i.e., the determination of the coefficients of the $C_p\left(T\right) = a_o + a_1 \cdot 10^{-3} T + a_{-2} \cdot 10^5 T^{-2}$ equation, was carried out by the method proposed in [6]. The values of the melting temperatures of $T_{melt}(K)$ compounds, indicators of standard S°_{298} entropies and temperatures of polymorphic transformations were used for the calculation. Tsagareishvili and Gvelesiani equation [7] was used to calculate the coefficients:

$$a = \frac{a_0}{n} = \left(5{,}95 - \frac{0{,}3 C^{hc}_{p298} \theta}{T_{melt}}\right); \tag{1.9}$$

$$b = \frac{a_1}{n} = \frac{0{,}34 C^{hc}_{p298}}{T_{melt}}; \tag{1.10}$$

$$c = \frac{a_2}{n} = 0{,}9\left(a + b \cdot 298 - C^{hc}_{p298}\right) \cdot 10^5; \tag{1.11}$$

where C^{hc}_{p298} – standard gram-atomic heat capacity, J/kg·K;

n – number of atoms in the compound, pcs.;

θ – characteristic temperature, K.

For some types of crystal compounds, in particular for intermetallics, a calculation method known in the scientific literature using the principles of the entropy method and the Kopp – Neumann rule is used [92]:

$$C_{p298} = 3{,}85 \lg S^{hc}_{298} + 2{,}25. \tag{1.12}$$

The characteristic temperature is determined by the formula [6]:

$$\theta = 1130\left(\exp\frac{S_{298}^{hc}}{3} - 0,78\right)^{-1/2}, \tag{1.13}$$

where S_{298}^{hc} – standard gram-atomic entropy, which can be calculated by the Yatsimirskii formula [7]:

$$S_{298}^{hc} = \frac{\sum S_{298\,el} - \alpha \cdot \Delta V}{n}, \tag{1.14}$$

where $\sum S_{298\,el}$ – the sum of the entropy of the elements that make up the compound, kJ/mol;

α – constant, when measured in ml/mol is approximately equal to 1/3;

ΔV – the difference between the volume of 1 mole of a compound and the sum of the atomic volumes of the components.

Melting points and polymorphic transformations are determined by the state diagram of the system of substances. The entropy values of the formed intermetallics are also missing, and can be calculated using Eastman's formula [8]:

$$S_{298}^{\circ} = R\left(\frac{3}{2}\ln A_{avg} + \ln V_{avg} - \frac{3}{2}\ln T_{melt}\right) + a, \tag{1.15}$$

where A_{avg} – the molecular mass of the compound, relative to the atoms in it;

V_{avg} – average atomic volume, m^3;

T_{melt} – the absolute melting point of the compound, K;

R – universal gas constant, which is equal to 8.31 J/mol · K;

a – constant, which is equal to 52.3 J/mol·K.

Formulas (1.12)–(1.14) determine the atomic heat capacity, characteristic temperature, and atomic entropy for intermetallic compounds of the *Ni-Al* and *Ti-Al* systems. Using the obtained data, the equations for determining the heat capacity were then obtained. The experimental values of $C_p(T)$ differed from the calculated data by no more than 5 %.

Based on the obtained heat capacity equations and reference data on the heat of formation, T_{ad} is calculated according to the expression (1.2). First, the thermal effect is calculated according to the formula [1–3]:

$$\Delta H\left(T_{mel}\right)=\int_{T_o}^{T_{mel}} C_p\left(T\right)dT, \tag{1.16}$$

and is compared with the Q magnitude. When $\Delta H(T_{melt}) > Q$ adiabatic temperature T_{ad} was lower than the melting point of the product T_{melt} and its value was found from the equation (1.2). If $\Delta H(T_{melt}) < Q$, then $T_{ad} \geq T_{melt}$, and in this case it is necessary to take into account the melting of the resulting product.

The heat of fusion of intermetallics is estimated by the formula [8]:

$$\Delta H_{p.t.} = \Delta S_{p.t.} \cdot T_{melt}. \tag{1.17}$$

Since it is known that entropy of the melting ΔS_{melt} non-organic compounds can be estimated within 5–7 cal/mol · deg (20,9–29,3 J/mol · K). Heat capacity of liquid product C_{fluid} was accepted equal to 8n cal/mol·deg, where n – the number of atoms in the molecule of the resulting compound.

Adiabatic combustion temperatures of binary metal systems that form various intermetallic compounds are given in **Table 1.1**.

Thermodynamic analysis showed that for most metal systems, the adiabatic combustion temperature is equal to or higher than the melting temperature of the final product, the intermetallic compound. This condition is sufficient for self-propagating high-temperature synthesis to occur in the system under normal conditions.

Therefore, the thermodynamic analysis of the thermochemical reactions of the formation of intermetallics based on the ratio of the adiabatic combustion temperature and the melting temperature of the resulting product showed that the researched reactions can be divided into two groups. The first group includes systems in which the adiabatic combustion temperature is lower than the melting temperature of the resulting compound ($T_{ad} < T_{melt}$).

Table 1.1. Adiabatic temperatures and enthalpy of intermetallic formation during thermochemical pressing [1–3]

Chemical compound	T_{melt}, **K**	ΔH°_{298}, **kJ/mol**	$\Delta H_{p.t.}$, **kJ/mol**	T_{ad}, **K**
Ni-Al				
$NiAl$	1911	–117,570	40,030	1911
Ni_2Al_3	1405	–288,696	29,430	1405
$NiAl_3$	1127	–150,624	23,610	1127
Ni_3Al	1668	–152,297	34,940	1566
Ti-Al				
$TiAl$	1733	–75,390	36,330	1654
$TiAl_2$	1273	–25,000	26,670	1171
$TiAl_3$	1613	–146,440	33,790	1517
Ti_3Al	1313	–98,320	27,510	1185

Firstly, it's a *Ti+Al system*, in which synthesis under normal conditions is unlikely. To carry out the synthesis reaction, preliminary heating is necessary. The second group includes systems for which the adiabatic combustion temperature is equal to or exceeds the melting temperature of the product formed ($T_{ad} \geq T_{melt}$). This group includes *Ni+Al* system, which, as shown by the thermodynamic calculation of the maximum adiabatic temperature, is characterized by interaction in the combustion mode under normal conditions.

1.1.2. Calculation of enthalpy of formation and Gibbs energy of intermetallics in a wide temperature range

Calculations are performed using the classical Van't – Hoff isotherm equation, reference data on standard values of enthalpy of formation of compounds, entropy, temperature series of heat capacities, as well as temperatures and thermal effects of phase transitions [9].

Thermodynamic calculations of the stability of intermetallic compounds, like other chemical compounds, are based on the use of Gibbs – Helmholtz equations, as a dependence of the change in Gibbs free energy on temperature [9]:

$$\Delta G_T = \Delta H_T^{\circ} - T \cdot \Delta S_T^{\circ}, \tag{1.18}$$

where ΔG_T – Gibbs free energy, kJ/mol;

ΔH_T° – enthalpy of formation, kJ/mol;

ΔS_T° – entropy, J/mol · K;

T – temperature, K.

In the event of an intermetallic formation reaction occurring in $Me - Al$system according to the equation:

$$Me_x + Al_y = Me_x Al_y, \tag{1.19}$$

the standard enthalpy of formation and entropy of this chemical reaction is calculated as follows [9]:

$$\Delta H_{298}^{\circ} = \nu_1 \sum \Delta H_{298\,prod}^{\circ} - \nu_2 \sum \Delta H_{298\,init}^{\circ}, \tag{1.20}$$

$$\Delta S_{298}^{\circ} = \nu_1 \sum \Delta S_{298\,prod}^{\circ} - \nu_2 \sum \Delta S_{298\,init}^{\circ}, \tag{1.21}$$

where $\sum \Delta H_{298\,cont}^{\circ}$ – sum of standard enthalpies of formation of reaction products, kJ/mol;

$\sum \Delta H_{298\,start}^{\circ}$ – sum of standard enthalpies of initial substances, kJ/mol;

$\sum \Delta S_{298\,cont}^{\circ}$ – sum of standard entropies of reaction products, kJ/mol;

$\sum \Delta S_{298\,start}^{\circ}$ – sum of standard entropies of initial substances, kJ/mol;

v_1 and v_2 – stoichiometric coefficients.

Next, for compound formation reactions $Me_x Al_y$ the Gibbs energy at standard temperature is calculated by formula (1.19).

Next, the change in enthalpy and entropy of intermetallics at the required temperature T [10] is calculated using the Kirchhoff equation:

$$\Delta H_T = \Delta H_{298}^{\circ} + \int_{298}^{T} \Delta C_p dT; \tag{1.22}$$

$$\Delta S_T = \Delta S^{\circ}_{298} + \int_{298}^{T} \frac{\Delta C_p dT}{T}, \tag{1.23}$$

where ΔC_p – change in heat capacity depending on temperature, J/mol · K.

The next step is to calculate the change in Gibbs energy (ΔG_T) of this intermetalide at temperature T:

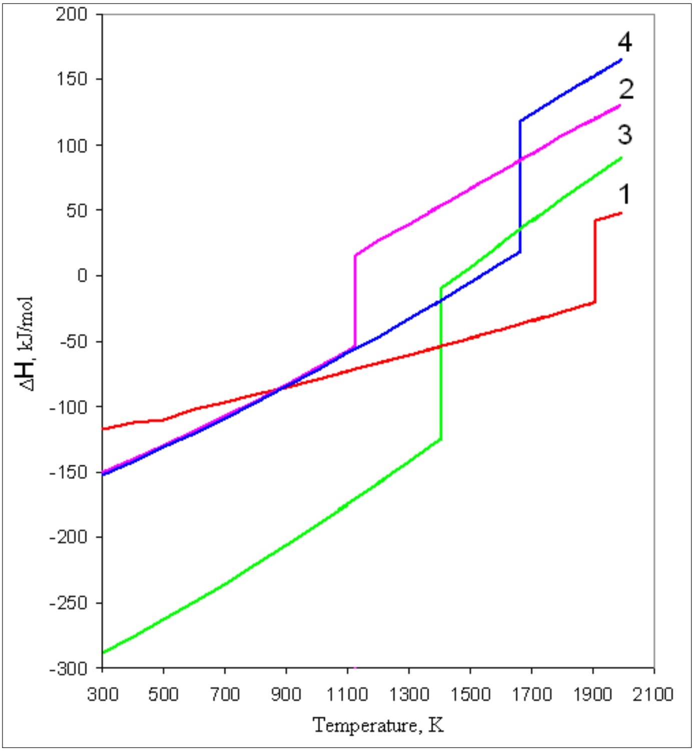
$$\Delta G_T = \Delta H_T - T \cdot \Delta S_T. \tag{1.24}$$

Calculations were carried out in a wide range of temperatures. The standard temperature of 298 K was chosen as the initial temperature for calculations, and the maximum melting temperature of intermetallics was chosen as the final temperature (~2000 K) [11]. For each intermetallic compound in the given temperature interval, the values ΔH_T and ΔG_T were calculated with misstep ~200 K. The values of the thermodynamic functions were also determined at the melting temperature of aluminum (933 K). For some compounds, calculations were performed using the «TERRA" program [12], which consists of an information fund and contains information on the thermodynamic properties of individual substances and a set of programs that calculate the parameters of the equilibrium state of chemically reacting systems.

The results of the calculated values ΔH_T and ΔG_T в інтервалі температур in temperature interval 298-T for chemical compounds, which are formed in dual systems based on aluminum (*Ti-Al, Ni-Al*), shown on Fig. 1.1 and 1.2.

Enthalpy calculations showed that in the temperature range $298 - T_{пл}$, K thermal effects of these chemical reactions amount to $\Delta H_T < 0$ and accordingly, the reactions occur with the release of heat (**Fig. 1.1–1.2**).

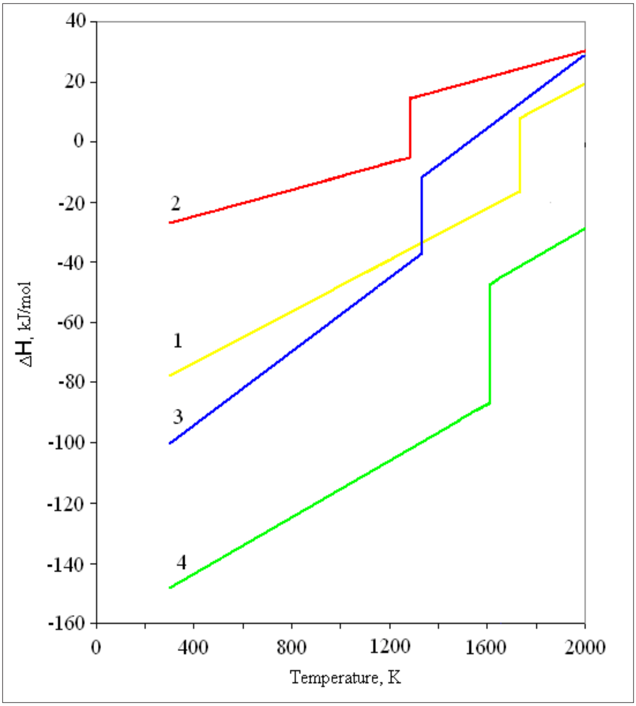
Analyzing the dependence of the Gibbs free energy on temperature, it is possible to draw a conclusion about the stability of intermetallic compounds that are formed in the *Ti-Al* and *Ni-Al* systems.



1 – NiAl; 2 – $NiAl_3$; 3 – Ni_2Al_3; 4 – Ni_3Al

Fig. 1.1. The results of calculating the thermodynamic properties of the formation of intermetallic alloys in the Ni-Al system

Each compound of the system is characterized by a negative value of Gibbs energy. The assessment of the change in Gibbs free energy ΔG_T during the formation of various aluminides with aluminum and nickel showed that in the entire temperature range, the intermetallic phase $NiAl_3$ has the lowest energy **(Fig. 1.3)**. Slightly lower ΔG in the Ni_2Al_3 metastable phase, but it can be formed only through several intermediate transformation reactions, which is thermodynamically unlikely.

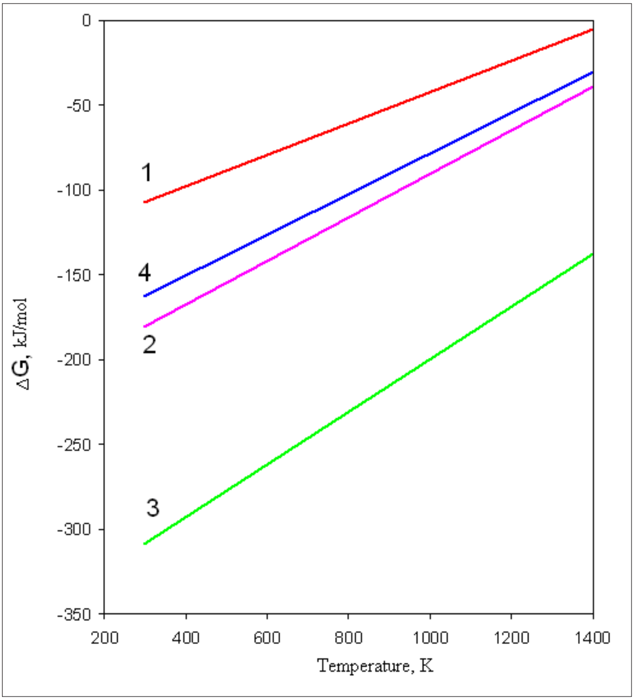


1 – $TiAl$; 2 – $TiAl_2$; 3 – $TiAl_3$; 4 – Ti_3Al

Fig. 1.2. Results of calculations of thermodynamic properties of the intermetallic Ti-Al system

Calculations of the change in Gibbs free energy ΔG during the formation of various aluminides from aluminum and titanium confirmed that the $TiAl_3$ phase has the lowest energy among stable intermetallics in the entire temperature range **(Fig. 1.4)**. Metastable phases $TiAl_2$ and Ti_2Al_5 have slightly lower ΔG, but they can be formed only through several intermediate transformation reactions, which is thermodynamically unlikely.

To calculate the equilibrium of chemical reactions in the studied systems, as well as to determine the equilibrium compositions of the



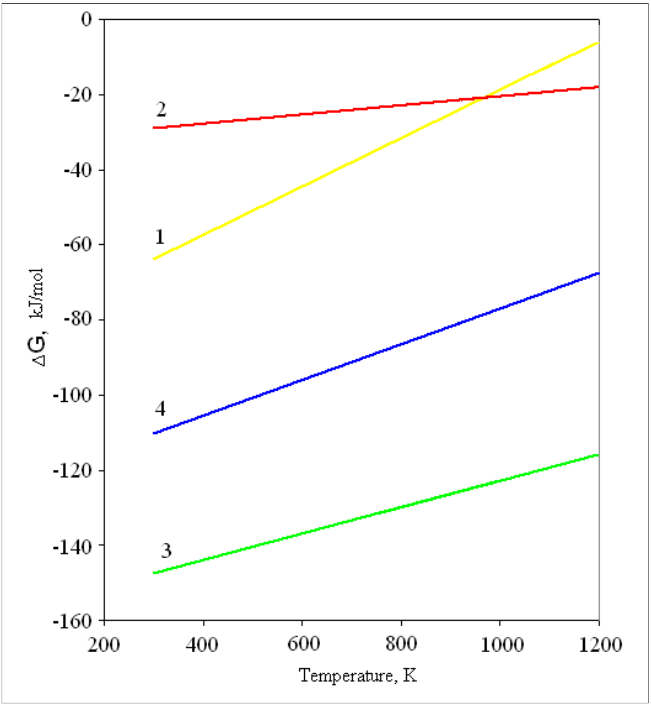
1 – NiAl; 2 – $NiAl_3$; 3 – Ni_2Al_3; 4 – Ni_3Al

Fig. 1.3. Change in Gibbs free energy ΔG in the *Ni-Al* system

components involved in these reactions, the equilibrium constants of all independent reactions possible in these systems were determined. The equilibrium constant is related to the change in the Gibbs energy of the reaction through the ratio [9, 10]:

$$\Delta G_T^o = -RT \ln k, \tag{1.25}$$

$$k_T = \exp\left(-\frac{\Delta G_T^o}{RT} \right). \tag{1.26}$$



1 – TiAl; 2 – $TiAl_2$*; 3 –* $TiAl_3$*; 4 –* Ti_3Al

Fig. 1.4. Change in Gibbs free energy ΔG in the *Ti-Al* system

Equations (1.25) and (1.26) make it possible, knowing ΔG^0, to calculate the equilibrium constant and, conversely, to determine the change in the Gibbs energy of the reaction based on the experimentally found value of the equilibrium constant. In fig. 1.5 and 1.6 present the results of the calculation of the reaction rate constant for the formation of intermetallic compounds in the *Ni-Al* and *Ti-Al* systems. The calculation results show that as the temperature increases, the value of the constant decreases, that is, heat is released as a result of reactions (a thermochemical reaction $Q > 0$ is exothermic).

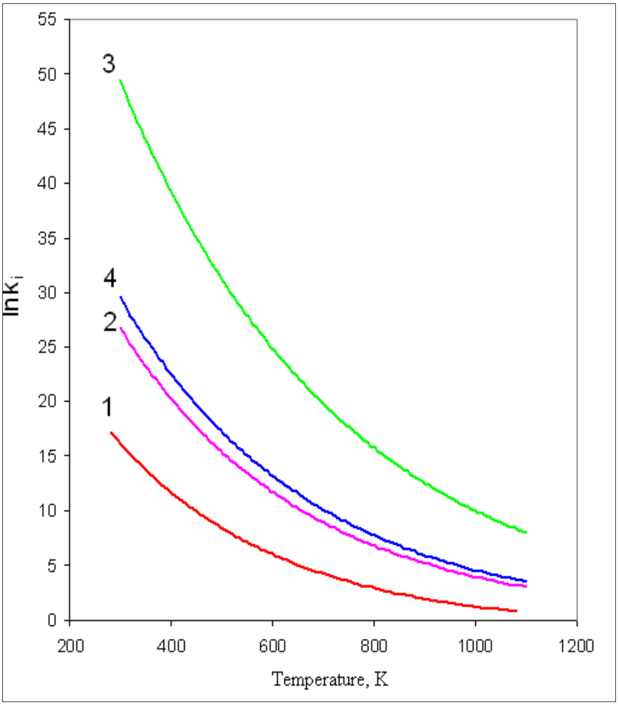
On the basis of the conducted thermodynamic calculation, it was established that the reaction of the formation of intermetallic compounds proceeds in a direct direction, at all possible temperatures of the process. Large values of the equilibrium constant (for *NiAl* $k = 5{,}03 \cdot 10^{18}$, *TiAl* $k = 2{,}3 \cdot 10^{11}$) show that under standard equilibrium conditions the reaction is highly shifted to the right, which means that at 298 K a stable intermetallic compound is formed. At low temperatures, below 933 K, the reaction proceeds very intensively, as evidenced by a very high value of the reaction constant.

The activation energy of each reaction can be estimated by the formula [9]:

$$E_a = \frac{R\left[\ln k_2 - \ln k_1\right]}{\frac{1}{T_1} - \frac{1}{T_2}}. \tag{1.27}$$

From the given dependences **(Fig. 1.5–1.6)**, we find the value of the reaction rate constant for the formation of intermetallic compounds at temperatures $T_1 = 298\ K$ and $T_2 = 100\ K$. Accordingly, we get for the *Ni-Al* system $\ln k_1 = 16{,}05$ and $\ln k_2 = 3{,}21$; for the *Ti-Al* system $\ln k_1 = 26{,}89$ and $\ln k_2 = 3{,}57$. The values of the activation energy of the formation of intermetallic alloys obtained by thermodynamic calculation were 45,153 kJ/mol and 82,263 kJ/mol, respectively.

Therefore, on the basis of thermodynamic analysis of the reactions of the formation of intermetallic alloys under the conditions of thermochemical pressing, the equilibrium constants of all independent reactions of the formation of intermetallics in the *Ni-Al* and *Ti-Al* systems and their activation energies were obtained. It was established that the activation energy for the reaction of the interaction of titanium and aluminum with the formation of intermetallics is 82.263 kJ/mol, which is ~ 1.8 times higher than the activation energy of *Ni-Al* alloys. Therefore, intermetallic compounds in the *Ti-Al* system have high values of activation energy, and therefore, show the complexity of thermochemical reactions under normal conditions.

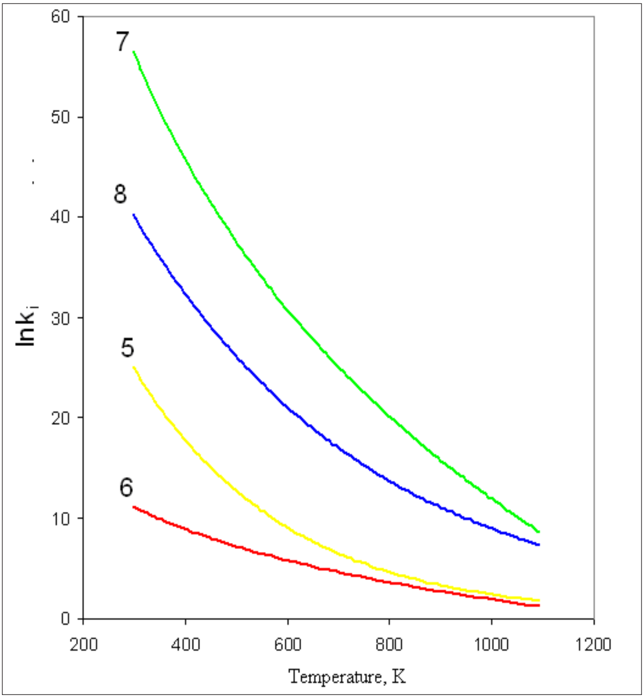


1 – NiAl; 2 – NiAl$_3$; 3 – Ni$_2$Al$_3$; 4 – Ni$_3$Al

Fig. 1.5. The results of the thermodynamic calculation of the reaction rate constant for the formation of intermetallic compounds in the *Ni-Al* system

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.

The second most important task of thermodynamics of thermochemical processes is aimed at calculating the equilibrium composition of synthesis products. Solving this problem allows you to find the composition of the reaction mixture necessary to obtain the desired product. Such thermodynamic analysis is especially important in complex multicomponent systems, when the composition

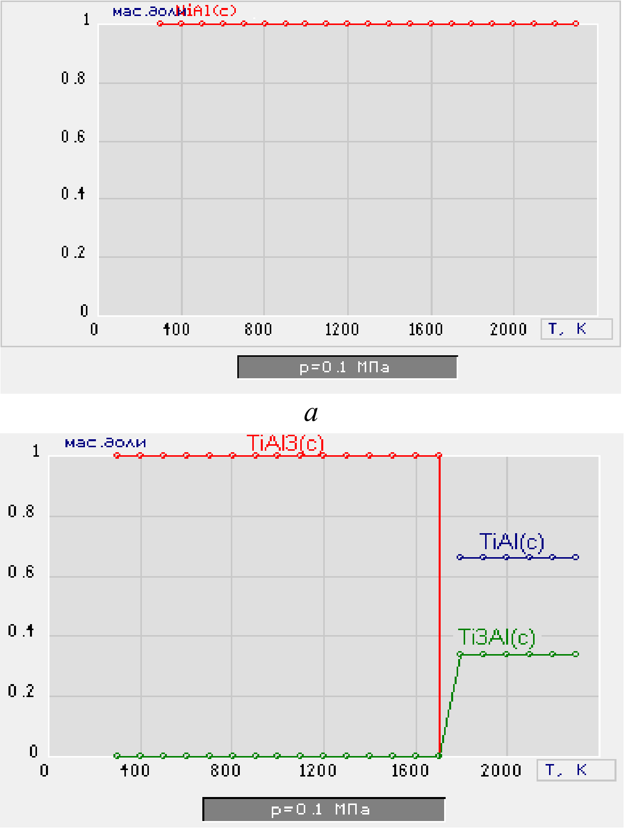


5 – TiAl; 6 – $TiAl_2$*; 7 –* $TiAl_3$*; 8 –* Ti_3Al

Fig. 1.6. The results of the thermodynamic calculation of the reaction rate constant for the formation of intermetallic compounds in the *Ti-Al* system

of combustion products is not obvious due to the presence of side competing reactions, phase transformations, dissociation. Conducted thermodynamic calculations of the change in Gibbs free energy ΔG during the formation of various aluminides from aluminum and titanium confirmed that the $TiAl_3$ phase has the lowest energy among stable intermetallics in the entire temperature range.

Fig. 1.7 calculated data of the equilibrium composition of the synthesis product in the *NiAl* and *TiAl* system are presented.



a

b

a – NiAl, b – TiAl

Fig. 1.7. Calculation of the equilibrium composition of intermetallics

Thermodynamic calculations of the equilibrium state in the *Ni-Al* system showed that intermetallics are always synthesized into a single-phase product of the specified stoichiometry. In the *NiAl* system, a single-phase product is formed – nickel monoaluminide *NiAl*. In the *TiAl* system, the calculation showed that although the target product of the reaction in this case is titanium monoaluminide *TiAl*, the main byproduct is the Ti_3Al phase. The ratio of phase components (*TiAl* to Ti_3Al) is 70:30 %. Therefore, the optimal areas for obtaining certain phases, determined thermodynamically (by calculation), will allow to monitor the processes of both phase formation and the formation of the microstructure of the product at all stages of the development of the process, to reveal the sequence of phase and structural transformations and the mechanisms of interaction of the specified metals with aluminum in the regime of high-temperature synthesis.

1.2. Thermokinetic analysis of thermochemical reactions

Thermodynamic admissibility of a thermochemical process is a necessary, but not yet sufficient condition for its implementation.

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). It is customary to write the temperature dependence of the rate of a chemical reaction in the form:

$$U = \sigma_n a \frac{c}{Q} \frac{RT^2}{E} k \exp\left(-\frac{E}{RT} \right), \tag{1.28}$$

where E – activation energy of this reaction, kJ/mol;

σ_n – a constant that depends on the order of the reaction (for example, for $n = 0$, $\sigma_n = 2$; for $n = 1$, $\sigma_n = 1{,}1$; for $n = 2$, $\sigma_n = 0{,}73$);

a – thermal conductivity, m^2/s;

k – coefficient, which includes a weak, compared to the exponent, 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:

$$\Phi(T) = k(1-\eta)^n \exp\left(-\frac{E}{RT}\right). \tag{1.29}$$

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.

1.2.1. Conditions of interaction of intermetallic systems at non-stationary temperature regimes

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. One of the options for conducting synthesis is heating at a given rate, which ends in a thermal explosion. 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.

The basics of the thermal explosion theory were developed by M. M. 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 [13]:

$$\dot{Q}_{chem} = Q\rho V k_0 e^{-\frac{E}{RT}} = Q\rho V k_0 \exp\left(-\frac{E}{RT}\right), \qquad (1.30)$$

where Q − thermal effect of the reaction, J/kg;

ρ – density of matter, kg/m^3;

V – volume of substance, m^3;

k_0 – pre-exponential multiplier, 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 a substance to the environment is determined by Newton's law:

$$\dot{Q}_{cool} = \alpha S\left(T - T_{env}\right), \qquad (1.31)$$

where α − heat transfer coefficient, W/(m^2 · K);

S − surface area of a substance, m^2.

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

In the stationary mode, $Q_{chem} = Q_{cool}$ thermal equilibrium is achieved: as much heat is released in the substance, as much heat is released into the environment. The temperatures reached in this mode are low, close to the environment temperature T_{env}. They are derived from the equilibrium equation: In the steady-state mode, thermal equilibrium is achieved: the amount of heat generated in the substance is equal to the amount dissipated into the environment. The temperatures reached in this mode are low, close to the ambient temperature. These temperatures are derived from the equilibrium equation:

$$Q\rho V k_0 \exp\left(-\frac{E}{RT}\right) = \alpha S\left(T - T_{env}\right). \qquad (1.32)$$

The stationary mode is established in the case of low values of the temperature of the environment T_{env}. and sufficiently strong heat dissipation into the environment.

In the case of high values of the environment temperature and weak heat dissipation, the equilibrium equation no longer has a solution, since here $Q_{chem} > Q_{cool}$ at any temperature $T > T_{env}$. 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 [14, 15].

M. M. Semenov 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 criterion of M. M. Semenov [13]:

$$Se = \frac{Q\rho V}{\alpha S}\frac{E}{RT_{env}^2}\exp\left(-\frac{E}{RT_{env}}\right), \tag{1.33}$$

$$Se_{crit} = \frac{1}{e} = 0{,}368.$$

If $Se < Se_{\mathrm{crit}}$ the process proceeds without explosion, if $Se > Se_{crit}$ a thermal explosion occurs. Knowing the kinetic and thermophysical properties of the reactant (Q, k_0, E, c, ρ), its shape and dimensions (V, S), as well as the conditions in which it is located (α, T_{evn}), you can easily calculate the value of the Semenov criterion S_e.

To implement the regime of thermal explosion of the substance, it is necessary to create the following conditions in the furnace (α, T_{evn}), in which the value of the Semenov criterion for this substance will be greater than the critical value Se_{crit}. As can be seen from formula (2.27) for this criterion, its value is greater, the larger the Q, ρ, V, k_0, T_{env} values and smaller the α, S values. Therefore, determining the activation energy of intermetallic *Ni-Al* and *Ti-Al* systems will allow to calculate the critical conditions and period of induction of these reactions.

1.2.2. Determination of the activation energy of Ni-Al and Ti-Al intermetallic systems

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. Having studied 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 μm) 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 [15–17]. With the help of numerous 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. 1.8**).

The calculated-analytical dependence of the formation of the first intermetallics in the *Ni-Al* system is presented in the form of an equation [18]:

$$\tau = 1{,}0 \cdot 10^{-4} \exp\left(\frac{42917}{RT}\right), \tag{1.34}$$

which allows determining the rate of formation of the first intermetallic phase regions [18]:

$$\dot{N} = 5{,}76 \cdot 10^{6} \exp\left(\frac{-42917}{RT}\right). \tag{1.35}$$

Therefore, the activation energy of the formation of the first intermetallic crystals according to experimental results is approximately 43 kJ/mol [19].

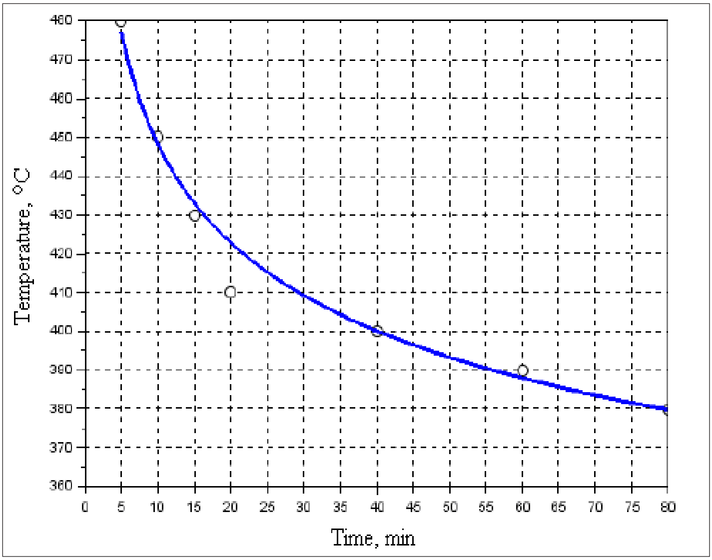


Fig. 1.8. Temperature-time dependence of the formation of intermetallics in the *Ni-Al* system

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 min of isothermal annealing. The temperature-time dependence of the appearance of intermetallics in the *Ti-Al* system is presented in **Fig. 1.9**. 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 [20, 21]. 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.

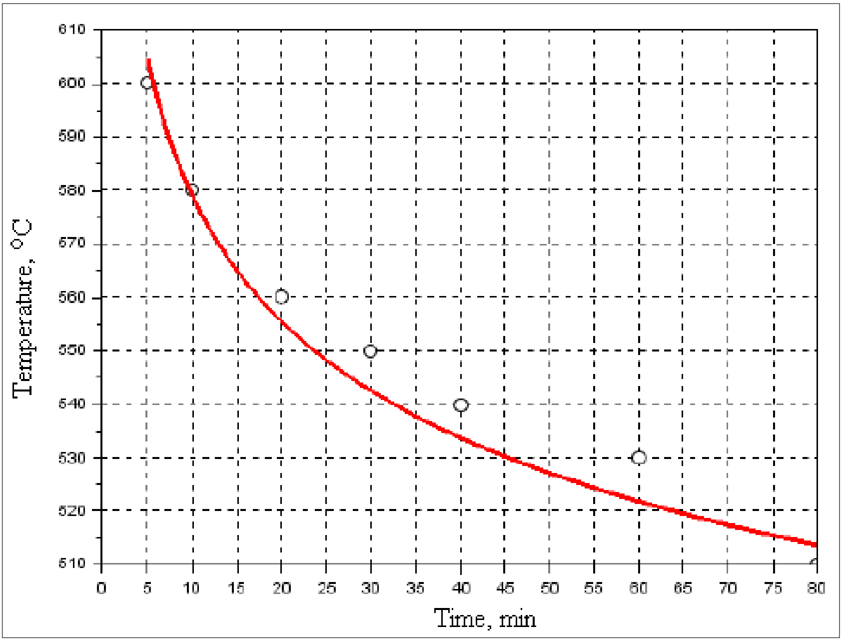


Fig. 1.9. Temperature-time dependence of the formation of intermetallics in the *Ti-Al* system

Calculation of the temperature-time dependence of the formation of the first intermetallics in the *Ti-Al* system allows us to determine the equation [18]:

$$\tau = 8{,}0 \cdot 10^{-7} \exp\left(\frac{78676}{RT}\right), \tag{1.36}$$

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 [18]:

$$\dot{N} = 7{,}2 \cdot 10^{8} \exp\left(\frac{-78676}{RT}\right). \tag{1.37}$$

Analytical equations of the temperature-time dependences of the formation of intermetallics in *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 thermochemical pressing. 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 activation energy values, and therefore show the complexity of thermochemical reactions 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 method of calculation 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 activation energy values obtained by two different methods does not exceed 5 % (**Table 1.2**) [19].

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

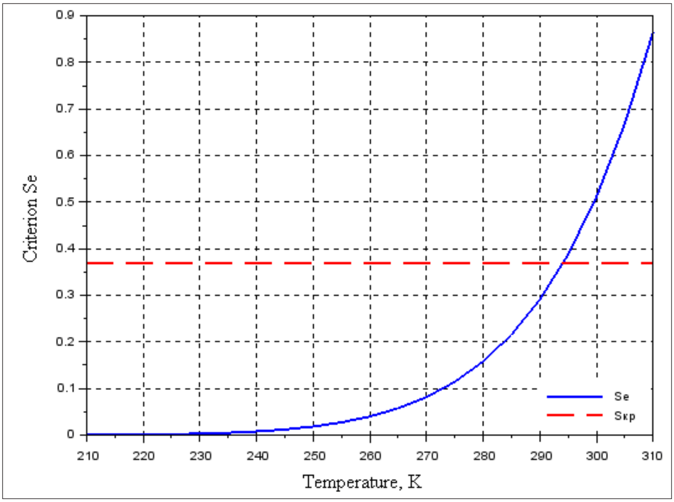
Table 1.2. Comparative analysis of calculations of activation energies obtained by different methods

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

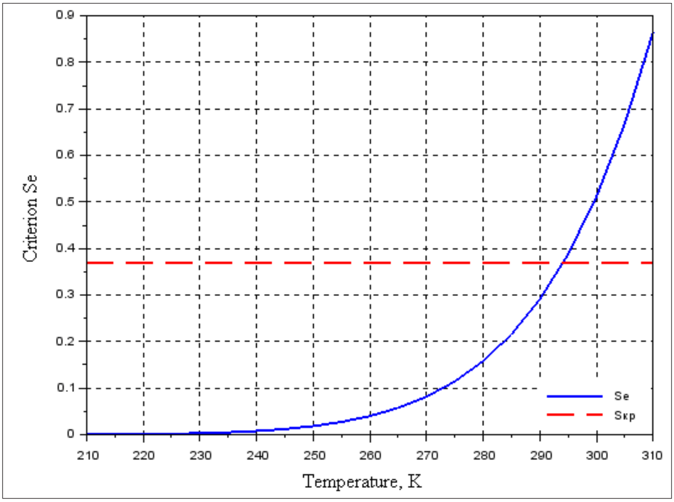
For the numerical solution of the thermal problem of the synthesis of titanium and nickel aluminide under the conditions of thermochemical pressing in the thermal model of M. M. Semenov, the following initial data were integrated:

- *Ni-Al* system:
  $Q_{NiAl} = 1{,}2 \cdot 10^3$ J/kg;
  $\rho_{NiAl} = 5870$kg/m^3;
  $V = 30 \cdot 10^{-3}$ m^3;
  $\alpha_{NiAl} = 400$ W/(m$^2 \cdot$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;
  $\rho_{TiAl} = 3800$ kg/m^3;
  $V = 30 \cdot 10^{-3}$ m^3;
  $\alpha_{TiAl} = 240$ W/(m$^2 \cdot$K);
  $S = 33{,}4 \cdot 10^{-4}$ m^2;
  $E_{TiAl =} 78676$ J/mol;
  $k_0 = 7{,}2 \cdot 10^8$ 1/s.

The analysis of the calculation results showed that for the *Ni-Al* intermetallic system, the calculated value of the criterion of M. M. Semenov above the critical (**Fig. 1.10**). This condition is sufficient for self-propagating high-temperature synthesis to occur in the system under normal conditions. Temperature analysis of intermetallic formation reactions according to the ratio of the calculation criterion M. M. Semenov and its critical importance showed that the investigated reactions can be divided into two groups. The first group includes systems in which the Semenov calculation criterion is lower than its critical value ($Se < Se_{cr}$).



a



b

a – Ni-Al, b – Ti-Al

Fig. 1.10. Dependence of the calculation of the M. M. Semenov criterion from the initial temperature of the synthesis of the intermetallic *Ni-Al* system

First of all, this is a *Ti+Al* system, in which the synthesis process 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 calculation criterion of M. M. Semenov equals 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.

1.2.3. Calculation of the depth of chemical transformation in the process of high-temperature synthesis

To determine the depth of transformation α, the Johnson-Mel-Avrami-Kolmogorov (JMAK) model was used, which allows us to estimate the kinetics of the formation of new phases and structural components. This model assumes that the appearance of a new phase occurs uniformly throughout the volume, the rate of appearance of a new phase does not depend on its already existing amount [22, 23]. The equation is written in the form:

$$\alpha(\mathrm{T}) = 1 - \exp(-K \cdot T^{n}), \tag{1.38}$$

where K – coefficient, which is determined by the growth rate of the phase in the volume and depends on the temperature and properties of a specific substance;

n – a parameter determined by the nature of crystallite growth.

Different values of n correspond to different conditions of embryo formation and growth. If the nuclei are preformed and therefore present from the beginning, the transformation occurs only through the three-dimensional growth of the nuclei, then $n = 3$.

The crystallite growth rate parameter K can be represented as:

$$K(\mathrm{T}) = \exp(-E_a / R \cdot T), \qquad (1.39)$$

since the crystallization process is thermally activated.

For the numerical solution of the thermal problem of the synthesis of nickel and titanium aluminides under the conditions of thermochemical pressing, the following initial data were integrated into the Johnson-Mel-Avrami-Kolmogorov kinetic model:

- *Ni-Al* system:
  $E_a = 42917$ J/mol,
  $\mathrm{T} = [530{:}-10{:}490$ °C],
  $k = 1{,}0 \cdot 10^{-4}$;
- *Ti-Al* system:
  $E_a = 78676$ J/mol,
  $T = [660{:}-10{:}620$ °C],
  $k = 8{,}0 \cdot 10^{-7}$.

The graphic interpretation of the obtained calculation results is presented in **Fig. 1.11** and **Fig. 1.12**.

Fig. 1.11 and Fig. 1.12 show time dependences of temperature and depth of chemical transformation in the process of high-temperature synthesis of *Ni-Al* and *Ti-Al* intermetallic systems. It was established that with a decrease in the temperature of the isothermal exposure, the rate of temperature growth and the depth of the transformation decrease.

Varying the temperature of synthesis, and therefore the speed of ignition, allows you to find the value at which the required degree of chemical transformation is achieved for the set time of synthesis [24]. In particular, for the *Ti-Al* system, at the ignition start temperature of 660 °C, the full depth of the chemical transformation is reached in 150 s, lowering the temperature to 620 °C leads to an increase in the synthesis time by ~2.5 times.

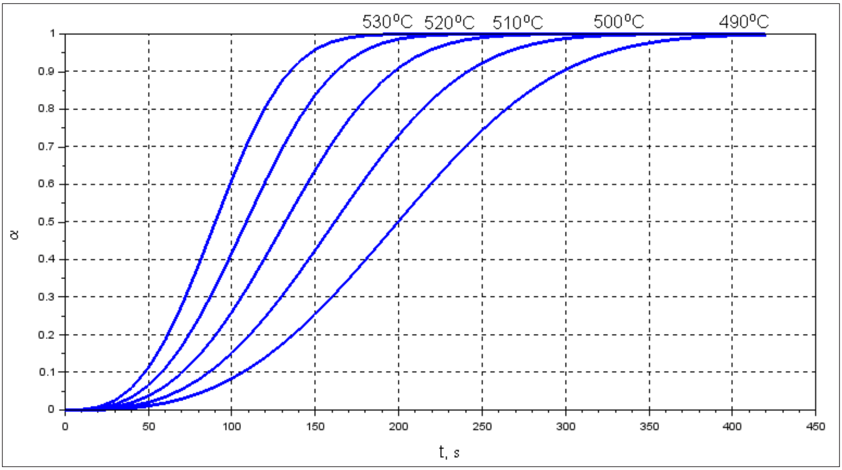


Fig. 1.11. Dependence of the depth of transformation (α) on the temperature and time of synthesis of intermetallics in the *Ni-Al* system

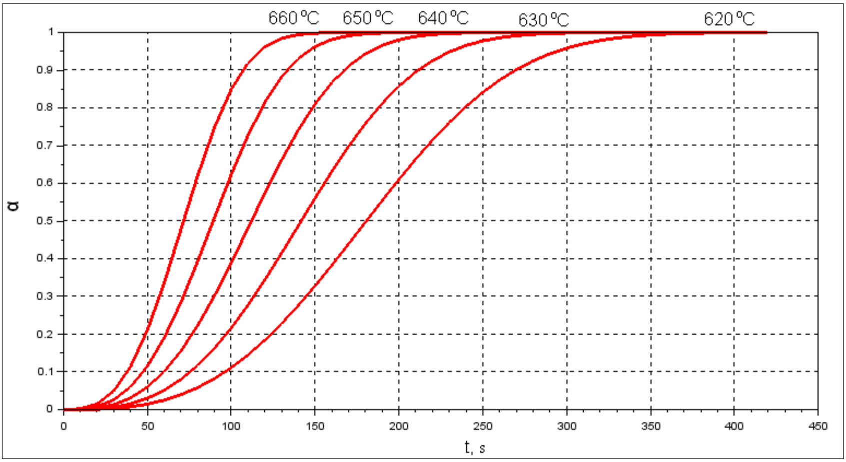


Fig. 1.12. Dependence of the depth of transformation (α) on the temperature and time of synthesis of intermetallics in the *Ti-Al* system

The calculation of the depth of the chemical transformation for the *Ni-Al* system showed that the temperature below the ignition limit is significantly lower than the *Ti-Al* system and is 530 °C, while the full depth of the chemical transformation is reached in 220 s, a decrease in temperature to 490 °C leads to an increase in the synthesis time ~ in 2 times.

1.3. Modeling the processes of structure formation of intermetallic alloys

To date, the concept of primary and secondary structure formation in thermochemical processes has already been formulated [25].

The initial reaction medium is a mixture of powders with a certain phase composition and microstructure, which are completely destroyed during the chemical reaction. As a result of the reaction, products are formed, the microstructure and phase composition of which are very different from the initial ones. The process of forming the structure of products during a chemical reaction is called primary structure formation, and the microstructure formed during this process is called the primary microstructure of the product. The characteristic time of the chemical reaction during synthesis is 10^{-3}–10^{-1} s, the same duration of primary structure formation. Heat release from a chemical reaction leads to self-heating of a heterogeneous medium to a temperature of the order of 2000–3500 K, while in most thermochemical systems, at least one initial reactant or reaction product melts. High temperature and the presence of a melt create favorable conditions for the processes of collective recrystallization (dissolution-precipitation and coalescence of grains), liquid-phase sintering, that is, they contribute to the further evolution of the product structure. All these processes occur after the end of the chemical reaction and are called secondary structure formation. The duration of this process depends on the cooling mode of the sample and is, as a rule, seconds and tens of seconds, but it can reach hours if the sample solidifies very slowly. The processes of secondary structure formation play a decisive role in the formation of the microstructure, crystal structure and phase composition of the target synthesis product.

It should be noted that the division into primary and secondary structuring is very conditional, and it is often difficult to draw a clear line between these stages. In particular, the combustion reaction itself can be multistage, therefore, during the primary structure formation, several products can be formed sequentially, some of which may be short-lived. On the other hand, the reaction does not always take place to the end in the combustion front. In many thermochemical systems, the combustion zone is followed by a wide pre-reaction zone, in which the chemical composition of the product slowly changes simultaneously with the processes of secondary structure formation. Taking into account all this, we can, however, claim that the separation of the stages of primary and secondary structure formation has a great methodological meaning for understanding the dynamics of the formation of the structure of synthesis products. This division is based on a fundamental difference in the driving forces of structure formation at various stages of thermochemical pressing: first it is a chemical reaction, and then it is a decrease in surface energy and the transition of the crystal structure to an equilibrium state. This difference persists even when the processes of primary and secondary structure formation partially overlap in time.

The study of primary structure formation is a difficult experimental task due to the rapidity of this process and the high temperature. In order to “freeze” the microstructure immediately after the end of the chemical reaction, it is necessary to cool the sample at a rate of 10^3–10^4 K/s. This cooling rate is achieved using special methods of cooling thin samples. A comparison of different hardening methods is carried out in [26] on the example of nitride systems.

Quenching, practiced in early works, in liquid nitrogen [27] allows samples to be cooled only at a rate of the order of 10^2 K/s. Such a small tempering rate is explained, apparently, by the formation of a steam-gas shell around the heated sample, which prevents intensive heat removal. Therefore, the hardening of wedge-shaped (or cone-shaped) samples in a massive copper block is more widely used today [26]. The reaction mixture is pressed into a wedge-shaped cutout of a massive copper block, which ensures rapid heat removal from the sample. Combustion is initiated at the wide base of the wedge and propagates in the narrowing channel. This leads to a gradual increase in specific heat loss, as a result of which the combustion front extinguishes before reaching a few millimeters to the edge of the wedge. The highest cooling rate, greater than 10^3 K/s, is achieved in the quench region, as the sample thickness in this region is minimal (typically 0.5–2.0 mm depending on the system). The microstructure in this area allows us to talk about the mechanism of primary structure formation. As it approaches the base of the wedge, the cooling rate of the products gradually decreases to a value of the order of 10^2 K/s. Therefore, the study of the microstructure along the entire length of the sample also allows obtaining information about the dynamics of secondary structure formation.

Another method of studying primary structure formation is based on model experiments of the “particle-foil” type [27]. The idea of the method is to simulate a separate reaction cell, for which individual particles of the reactant are placed on a thin substrate (foil) made of another reactant, which is heated by electric current.

The heating mode is set as close as possible to the thermal mode of the combustion wave. The particle melts and begins to actively interact with the foil, and at any moment this interaction can be interrupted by simply turning off the electric current. Due to the thickness of the foil (50–200 μm), cooling occurs at a rate of about 10^4 K/s, which allows to “freeze” the primary microstructure. In addition, the simple geometry of the particle-foil reaction cell simplifies the analysis of interaction mechanisms compared to a real powder mixture, in which interparticle contacts are random. In the contact zone of the reagents, the melting of the foil and the chemical spreading of the melt occur with the simultaneous formation of a thin layer of submicron grains on the surface of the substrate. Therefore, during the primary structure formation, a refractory reactant dissolves in the melt of another reactant (or contact melting) and solid grains of the product fall out of the supersaturated melt.

A somewhat different picture of primary structure formation is observed in intermstalid systems. If both metal reagents melt in the combustion front, many small droplets coalesce into large globules, inside which the reagents are mixed due to convection and diffusion. Such a reaction mechanism was named reactive coalescence [26]. The primary product can be a melt (if the combustion temperature exceeds the melting point of the product), a solid polycrystalline material with a relatively uniform structure. The reaction diffusion mechanism is also known [28], which leads to the formation of a solid product layer at the interface of the reactants. As a rule, this mechanism can be observed in systems with one non-fusible reactant whose particle sizes exceed several micrometers.

Despite the fact that the actual combustion ends with the formation of the primary product, the evolution of the structure of this product continues behind the combustion front, during post-burning and cooling of the samples. This is facilitated by the high temperature behind the combustion front, the small size of primary grains (i.e., high surface energy), and the presence of melts. The main processes of secondary structure formation are: grain growth, ordering of the crystal structure, more uniform distribution of elements (pre-reaction). The last of the mentioned processes is of the greatest importance for multicomponent systems containing refractory additives that dissolve relatively slowly in the main phases. The issue of product equilibrium is directly related to the problem of secondary structure formation. Indeed, the natural cooling of small (up to 2–3 cm thick) samples after gasless combustion usually lasts from several seconds to several minutes. Therefore, the question of whether an equilibrium phase composition and an equilibrium structure of products can be formed in such a short time is quite relevant, and what will happen if the time of stay of products at high temperature is artificially extended. The noted aspects of secondary structure formation are considered below. A general feature in the combustion of stoichiometric compositions is a wide spread of concentrations at the boundary with the combustion zone and its gradual narrowing as combustion progresses. At the same time, the average composition of the product gradually approaches stoichiometric. In the case of a non-stoichiometric composition at the boundary of the homogeneity region, the composition of the primary product is closer to the composition of the final product, and the dispersion of concentrations in the afterburning zone is not so great. Apparently, the composition of the primary product is determined by the composition of the matrix melt in which the crystallization of this product takes place. In the *Ti-C* system, carbide grains are formed in the titanium melt (in which carbon is dissolved), so the carbide in the afterburning zone contains, on average, more titanium and less carbon compared to stoichiometry. As a result of the pre-reaction measurement, the concentrations are equalized over the entire volume of the product, the composition of the phases approaches equilibrium – TiC for the $Ti + C$ mixture and $TiC_{0,5}$ for the $Ti + 0.5C$ mixture. In the *Ni-Al* system, both reagents melt, and in the reaction zone fusion and mutual mixing of melts takes place (reaction coalescence). The regularities of this process have not been studied yet, but, apparently, the crystallization of the product begins first in those areas of the melt that are enriched with a more refractory component – nickel (which also agrees with the state diagram). Therefore, in the reaction zone, the nickel monoaluminide phase with a reduced aluminum concentration crystallizes, and in the afterburning zone, the solid product is saturated with aluminum.

The processes of secondary structure formation strongly influence the composition, shape and size of structural components. This opens up possibilities for effective management of the structure of products, since it is easy to influence relatively slow processes of secondary structure formation compared to extreme processes in the wave front of a thermochemical reaction.

An important issue is the effect of the composition of the powders of the initial mixture, its dispersion and temperature regime on structure formation in the binary system. The thermal explosion in heterogeneous systems interacting by the mechanism of reaction diffusion in a cylinder reactor was considered, taking into account the dynamics of melting of the low-melting component. Based on the numerical solution of the heat conduction equations for the cylinder reactor and the diffusion equations of the low-melting component in the lattice of the refractory component in the volume of the mesocell, it was established that in the process of self-heating behind the melting front, the temperature rises, while a low-temperature combustion wave is formed on the plane of which has there is a phase formation process with a low burnout depth. At the moment when the melting front reaches the geometric center of the reactor, there is a rapid increase in temperature (thermal explosion), which is accompanied by a sudden change in the depth of burnout in the center. Next, the front of complete transformation moves to the periphery of the cylinder, while the speed of the front slows down. Depending on the thermophysical parameters of the problem, either complete burnout of the components along the radius of the cylinder may occur, or the full transformation front stops and incomplete burnout of the components along the radius of the cylinder occurs.

The macrokinetics of self-heating and the completeness of the transformation are most significantly affected by two parameters, the first of which [25]:

$$\alpha(t) = \frac{3\rho_1 \cdot Q \cdot E}{R \cdot T_1^2 \cdot c_2 \cdot \rho_2}, \tag{1.40}$$

where ρ_1 – liquid phase density, g/cm^3;

Q – thermal effect of phase formation;

T_1 – melting point of the low-melting component, K;

C_1, C_2 – effective heat capacity and density of the medium from the particles of the refractory component and the liquid phase, J/K.

The second factor is the Bio criterion:

$$Bi = \alpha R / \lambda ,$$

where α – heat transfer coefficient, W/m² · K;

R – the inner radius of the cylinder, m;

λ – thermal conductivity of the cylinder material, W/m · K [29].

It was established that the completeness of the burnout in terms of the volume of the reactor depends on the Bio criterion. In the case of small values of the specified criterion, even in the case of a low-exothermic reaction, a complete transformation of the components occurs in the reactor volume with a high uniformity of product distribution in the reactor volume.

On the basis of the previously described ideas, modeling of the processes of structure formation in the *Ti-Al* system during self-heating in the mode of thermal explosion was carried out and the dependence of the phase composition of the final product on the ratio of components and thermophysical conditions of synthesis was determined based on the state diagram. When constructing the model, it was assumed that the heat release from the processes that occur during the diffusion recrystallization of the α-solid solution into the β-solid solution and the decomposition of the α_2-phase is neglected compared to the thermal effects of the reaction. The main goal of the calculation was to clarify the qualitative regularities of the structure formation processes during the synthesis of titanium aluminides in the thermal explosion mode for *Ni+Al* and *Ti+Al* systems with different dispersity of the particles of the refractory component [30, 31].

In this problem, using the example of *Ti-Al*, the self-heating of a powder mixture located in a reactor of volume V with a heat transfer surface S with an effective heat transfer coefficient α was considered. The problem was analyzed in a thermally gradientless formulation, with $Bi<<1$. It was assumed that self-heating occurs under static conditions, with a fixed temperature of the reactor wall throughout the synthesis process, which is higher than the melting temperature of the low-melting component. Melting and the mixture reaching the wall temperature T^* in the system does not form phases, the low-melting component is completely in the liquid phase. The ratio of the components, corresponding to the stoichiometry of the $TiAl_3$ and $TiAl$ phases, was considered, and accordingly, the size of the reaction cell was calculated according to the well-known formula [25]:

$$R_e = r_{Ti}\left(1+\frac{\mu_{Al}\vartheta_{Al}\rho_{Ti}}{\mu_{Ti}\vartheta_{Ti}\rho_{Al}}\right)^{\frac{1}{3}}, \tag{1.41}$$

where r_{Ti} – radius of the titanium particle, m;

μ_{Ti}, μ_{Al} – atomic (molar) masses of aluminum and titanium, respectively, dalton (g/mol);

ϑ_{Ti}, ϑ_{Al} – stoichiometric coefficients;

ρ_{Ti}, ρ_{Al} – density of aluminum and titanium, g/cm^3.

The heat balance equation for a powder system with liquid aluminum:

$$C_V\frac{dT}{dt} = nW^+ - \alpha\frac{S}{V}(T-T^*), \tag{1.42}$$

where C_V – heat capacity per unit volume of the mixture, J/K;

T^* – reactor wall temperature, K;

n – number of cells per unit volume, piece;

W^+ – fluidity of thermal imaging, which is indicated by the fluidity of phase formation, as well as the fluidity of dissolution, m/s.

The maximum synthesis temperature did not reach the melting temperature of the $TiAl_3$ phase, so the reasons for the heat transfer to melting were not clear.

The expression for the heat release rate has the form [29]:

$$W^+ = Q_1\rho_{Al}\frac{dI_1}{dt} + Q_2\rho_{Al}\frac{dI_2}{dt} + Q_3\rho_{Al}\frac{dI_3}{dt} - \\ -4\pi r_1^2\left(c_l\frac{dr_1}{dt} - D_l\frac{\partial c}{\partial r}\Big|_{r_1+0}\right)Q_l\rho_{Al}, \tag{1.43}$$

where Q_1 – thermal effect of $TiAl_3$ phase formation, kJ/mol;

Q_2 – *TiAl phase*;

Q_3 – Ti_3Al phase (per unit mass of aluminum);

$r_1(t)$ – the current radius of the particle in the process of phase formation, *m*:

$$r_0 \le r_1 \le R_e;$$

c_1 – experimental aluminum concentration;

$D_l = D_{0l}\exp\left(-E_i/RT\right)$ – diffusion coefficient in the liquid phase (D_{0l} – pre-exponent, E_i – activation energy, kJ/mol);

I_1 – amount of aluminum in the phases.

$$I_1 = 4\pi\int_{r_2}^{r_1} c(r)r^2dr,$$

$$I_2 = 4\pi\int_{r_3}^{r_2} c(r)r^2dr,$$

$$I_3 = 4\pi\int_{r_4}^{r_3} c(r)r^2d. \tag{1.44}$$

System of diffusion equations in areas [25, 29]:

$$r_1 < r < R_e,$$

$$\frac{\partial c}{\partial t} = D_l\left(T\right)\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c}{\partial r},$$

$$r = r_{1+0},$$

$$c = c_l,$$

$$r = R_e \text{ (melting); (1.45)}$$

$$r_2 < r < r_1$$

$$\frac{\partial c}{\partial t} = D_1\left(T\right)\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c}{\partial r},$$

$$r = r_{1-0},$$

$$c = c_1,$$

$$r = r_{2+0},$$

$$c = c_2 \ (TiAl_3);$$

$$r_3 < r < r_2,$$

$$\frac{\partial c}{\partial t} = D_2\left(T\right)\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c}{\partial r},$$

$$r_4 < r < r_3,$$

$$c = c_{3.}$$

$$r = r_{2-0},$$

$$c = c_4,$$

$$r = r_{3+0} \ (TiAl);$$

$$\frac{\partial c}{\partial t} = D_3\left(T\right)\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial c}{\partial r},$$

$$r = r_{3-0},$$

$$c = c_5,$$

$$r = r_{4+0},$$

$$c = c_6 \ (Ti_3Al);$$

$$0 < r < r_4,$$

$$\frac{\partial c}{\partial t} = D_4 \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial c}{\partial r},$$

$$r = r_{4-0},$$

$$c = c_7,$$

$$r = 0,$$

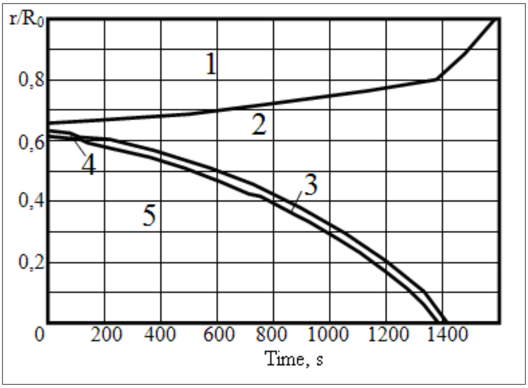
$$\frac{\partial c}{\partial r} = 0\,.$$

All diffusion coefficients are determined using the Arrhenius dependence $D_l = D_{0l} \exp(-E_i/RT)$ from temperature.

On the basis of the considered models, the mechanisms of structure formation in the Ni+Al and Ti+Al systems were determined, which, as it turned out, are qualitatively different. The study was performed using thermodynamic modeling methods [30, 31]. The thermodynamic equilibrium model is widely used in scientific and industrial practice when studying the behavior of chemically complex systems at elevated temperatures, when chemical or phase transformations play an important role. In chemical-technological processes, the main task of modeling is to determine the composition of phase components. The “TERRA” system for modeling phase and chemical equilibria [12] was used as software.

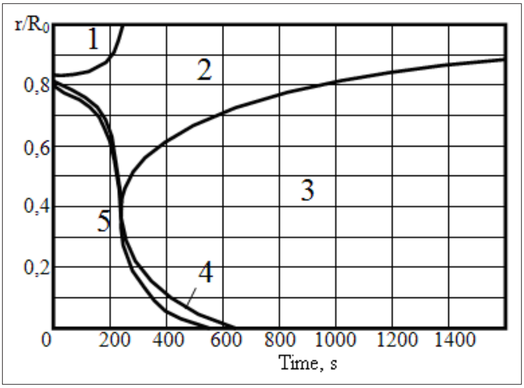
Fig. 1.13 and **Fig. 1.14** show characteristic results of the calculation of the dynamics of the structure formation process for the Ni+Al and Ti+Al systems. Here, the abscissa axis is time, the ordinate axis is mass. fate of the synthesis product.

The given results correspond to the particle size of the refractory component of 100 μm. In the synthesis of the $NiAl$ compound, at any value of the heat transfer coefficient less than the critical one,



1 – melting; 2 – NiAl; 3 – $NiAl_3$; 4 – Ni_2Al_3; 5 – solid solution

Fig. 1.13. Dynamics of phase formation in the *Ni-Al* system in the cell volume



1 – melting; 2 – Ti_3Al; 3 – TiAl; 4 – $TiAl_3$; 5 – solid solution

Fig. 1.14. Dynamics of phase formation in the *Ti-Al* system in the volume of the cell

it is always synthesized into a single-phase product of the specified stoichiometry. In this system, the formation of a single-phase product occurs by means of diffusion recrystallization of the $NiAl_3$ phase and the Ni_2Al_3 phase into the *NiAl* intermetallic. The recrystallization process ends when the maximum synthesis temperature is reached.

When interacting in the $Ti + Al$ system, as in the previous case, at the first stage there is a rapid process of formation of the $TiAl_3$ phase with the simultaneous disappearance of the melt, which corresponds to reaching the maximum temperatures. However, the amount of aluminum is not sufficient for the formation of titanium trialuminide, which causes the interface of the specified phase with the $TiAl$ phase to stop. A decrease in the aluminum concentration gradient in the region of the $TiAl_3$ compound, caused on the one hand by the diffusion of aluminum deep into the particle, on the other hand by the condition of cell boundary impermeability, leads to the movement of the front in the direction of the periphery of the cell, therefore, after stopping, the front "returns" and diffusion recrystallization of titanium trialuminide occurs into the γ-phase.

At the same time, recrystallization of the $\alpha 2$-phase and solid solution occurs. In contrast to the synthesis of nickel aluminide, diffusion processes occur more slowly, and the synthesis of the γ-phase occurs during cooling, with slow movement of the interface and with weak heat release (repeated structure formation). When synthesizing in the $Ti+Al$ system to obtain a single-phase product, the synthesis must be carried out with an annealing duration of at least 3000 s for a large fraction of titanium particles. For a finer fraction (less than 100 μm), an annealing time of about 1800 s (30 min) is required.