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MODELING AND THERMODYNAMIC ANALYSIS OF REACTIONS DURING THERMOCHEMICAL PRESSING OF POWDER INTERMETALLIC ALLOYS

The results of thermodynamic analysis of reactions that are possible during the production of powder intermetallic alloys under the conditions of thermochemical pressing are presented. On the basis of thermodynamic analysis of the course of reactions of formation of intermetallic alloys in the conditions of thermochemical pressing the thermodynamic properties and equilibrium constants of all independent reactions of formation of intermetallics in Ni-Al and Ti-Al systems and their activation energies are obtained. It was found that intermetallic compounds in the Ti-Al system have high values of activation energy, and therefore show the complexity of thermochemical reactions under normal conditions. The equilibrium composition of the synthesis product in the Ti-Al system, although the target reaction product here is titanium monoaluminide г-TiAl, but the main (inevitably present) by-product is б$_2$*-Ti*$_3$*Al.*

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

Представлено результати термодинамічного аналізу реакцій, що можливі під час одержання порошкових інтерметалідних сплавів за умов термохімічного пресування. На основі термодинамічного аналізу перебігу реакцій утворення інтерметалідних сплавів в умовах термохімічного пресування отримані термодинамічні властивості та константи рівноваги всіх незалежних реакцій утворення інтерметалідів у системах Ni-Al і Ti-Al та їхні енергії активації. Встановлено, що інтерметалідні сполуки в системі Ti-Al мають високі значення енергії активації, а відтак, показують складність перебігу термохімічних реакції в звичайних умовах. Рівноважний склад продукту синтезу у системі Ti-Al хоча і цільовим продуктом реакції тут є моноалюмінід титану г-TiAl, але основним (неминуче присутнім) побічним продуктом є б$_2$*-Ti*$_3$*Al.*

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

Problem's Formulation

Thermodynamic analysis, first of all determination of maximum adiabatic temperatures of process, acquires essential value at an estimation of possibilities of reception of various inorganic compounds, in particular aluminides, by a method of thermochemical pressing. A significant amount of data from thermodynamic analysis of reactions of 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 in the reference literature on their thermodynamic properties, such as heat capacity and entropy. At the same time, various empirical and semi-empirical methods for estimating these values are known. Therefore, it is of undeniable interest to conduct thermodynamic analysis of intermetallic formation reactions using such methods that allow to estimate unknown quantities with a sufficient level of accuracy.

Further progress in the creation of intermetallic alloys is possible with the use of new methods of synthesis. One of the most promising areas in the field of obtaining new materials with a high level of performance is the creation of composite materials based on intermetallics by high-energy and highspeed pressure treatment methods. Such technologies are the technology of thermochemical pressing. Thermochemical pressing is a new type of technology for processing metals by pressure, in which hot products of thermochemical synthesis, which have not yet cooled, are compacted by external forces (pressing, extrusion, blasting) [1, 2].

Given the above, the aim of this work was to study the effect of thermodynamic properties of intermetallic systems on the structure and phase formation of alloys obtained by thermochemical pressing of powder mixtures of Ni-Al and Ti-Al systems.

Analysis of recent research and publications

The object of research is intermetallic alloys based on titanium and nickel aluminides. Thermodynamic calculations were performed in a wide range of temperatures. The initial temperature for calculations is the standard temperature of 298 K, and the final — the maximum melting point of intermetallics (~ 2000 K) [3]. For each intermetallic compound in this temperature range, the values of and were calculated in increments of ~ 200 K. The values of the thermodynamic functions were also determined at the melting point of aluminum (933 K). For some compounds, calculations were performed using the programs "TERRA" and "THERMO" [4], which consists of an information fund and contains information about the thermodynamic properties of individual substances and a set of programs that calculate the equilibrium parameters of chemically reactive systems. Calculations of enthalpy of formation and Gibbs energy of intermetallics in a wide temperature range were performed using the classical Vant-Hoff isothermal equation, reference data on standard values of enthalpy of formation of compounds, entropy, temperature series of heat capacities, and temperature and thermal effects of phase transitions [5].

Formulation of the study purpose

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 provide an intense heterogeneous response. It is desirable that the adiabatic combustion temperature be higher than the melting point of at least one of the components. Therefore, consider briefly the method and results of calculating the combustion temperature.

Presenting main material

Temperatures of thermochemical processes are usually calculated under the assumption of adiabaticity, ie the absence of heat loss from the reaction zone, in the case of complete conversion of reagents into final products. At the same time the equality of enthalpies of initial substances at initial temperature T_o and final products at $T_{ад}$ [6] should be carried out

$$\sum_{i=1}^{n}\left[H(T_{ад})-H(T_o)\right]_i=\Delta H=Q_x, \tag{1}$$

where $T_{ад}$, T_o — adiabatic and initial reaction temperatures; Q_x — thermal effect of the reaction. Data are summarized for all reaction products.

If one product is formed, equation (1) takes the form

$$\int_{T_o}^{T_{ад}} C_p(T)dT=Q-\mu\cdot L, \tag{2}$$

where $C_p(T)$ — heat capacity; Q, L — heat of formation and melting of the product, respectively; μ — the proportion of the liquid phase in the combustion product;

$$\mu=\begin{cases}0 & \text{при } T_{ад}<T_{пл}\\ 1 & \text{при } T_{ад}>T_{пл}\end{cases}. \tag{3}$$

If, $T_{ад}=T_{пл}$ then $0<\mu<1$. The fraction of the high-temperature phase for the case $T_{ад}=T_{пл}$ can be determined by the formula

$$\mu=\frac{Q-\bar{c}(T_{пл}-T_0)}{L}, \tag{4}$$

where $\bar{c}$ — the heat capacity of the reaction products, averaged over the temperature range $T_0 \ldots T_{ад}$.

In the simplest case of one reaction product formed of elements

$$\sum_{i=1}^{n} X_i \to Z . \qquad (5)$$

Then equation (1) can be transformed by equation (2). Usually the values $T_{ад}$ are found from the solution of equation (2). Using the expression for the average heat capacity and thermal effect of the process

$$\bar{c} = \frac{1}{T_{ад} - T_0} \int_{T_0}^{T_{ад}} c(T)dT ; \qquad (6)$$

$$\overline{Q} = Q - \mu \cdot L , \qquad (7)$$

can be rewritten (2) for greater clarity in the form

$$T_{ад} \approx T_0 + \frac{\overline{Q}}{\bar{c}} . \qquad (8)$$

A number of papers have used a more general approach that considers the chemical and phase equilibrium in multicomponent combustion products and allows to calculate not only the combustion temperature but also the composition of products [5, 7]. For gas-free 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 compounds ΔH_{298}, temperature dependences of their heat capacity $C_p(T)$, heat of fusion. L.

he greatest difficulties in thermodynamic analysis arise due to the lack of study of temperature dependences of the heat capacity of the formed compounds. The heat of formation of a significant amount of these compounds is given in the reference literature [7, 8]. Approximate semi-empirical methods are used to obtain the equations for determining the heat capacity and heat of fusion. There are several methods for calculating the heat capacity of compounds, such as Neumann-Kopp, Landia and others. The calculation of heat capacity, ie determination of the coefficients of the equation $C_p(T) = a_o + a_1 \cdot 10^{-3} T + a_{-2} \cdot 10^5 T^{-2}$, was performed by the method proposed in [90]. The values of melting points of compounds $T_{пл}(K)$, indicators of standard entropies S°_{298} and temperatures of polymorphic transformations were used for calculation. Tsagareishvili and Gvelesiani equations were used a_0, a_1, a_{-2} to calculate the coefficients [9]

$$a = \frac{a_0}{n} = \left(5{,}95 - \frac{0{,}3C^{am}_{p298}\theta}{T_{пл}}\right); \qquad (9)$$

$$b = \frac{a_1}{n} = \frac{0{,}34C^{am}_{p298}}{T_{пл}}; \qquad (10)$$

$$c = \frac{a_2}{n} = 0{,}9\left(a + b \cdot 298 - C^{am}_{p298}\right) \cdot 10^5 , \qquad (11)$$

where C^{am}_{p298} — standard gram-atomic heat capacity; n — the number of atoms in the compound; θ — characteristic temperature.

For some types of crystalline compounds, in particular for intermetallics, the method of calculation C_{p298} known in the scientific literature using the principles of the entropy method and the Kopp-Neumann rule is used [10]

$$C_{p298} = 3{,}85\, lg\, S^{am}_{298} + 2{,}25 . \qquad (12)$$

The characteristic temperature is determined by the formula [13]

$$\theta = 1130\left(exp\frac{S_{298}^{am}}{3} - 0{,}78 \right)^{-1/2}, \tag{13}$$

where S_{298}^{am} — standard gram-atomic entropy, which can be calculated by the formula of Yatsimirsky [9]

$$S_{298}^{am} = \frac{\sum S_{298\,эл} - \alpha \cdot \Delta V}{n}, \tag{14}$$

where $\sum S_{298\,эл}$ — sum of entropies of the elements that make up the compound; α — constant, when measured in ml/mol is approximately 1/3; ΔV — the difference between the volume of 1 mole of the compound and the sum of the atomic volumes of the components.

Melting points and polymorphic transformations are determined by the state diagram. Also, the missing values of the entropy of intermetallics formed can be calculated by the formula of Eastman [11]

$$S_{298}^{\circ} = R\left(\frac{3}{2}\ln A_{cp} + \ln V_{cp} - \frac{3}{2}\ln T_{пл} \right) + a, \tag{15}$$

A_{cp} — molecular weight of the compound relative to the atoms in it; V_{cp} — average atomic volume; $T_{пл}$ — absolute melting point of the compound; R — universal gas constant, which is equal to 8.31 J/(mol·K); a — constant equal to 52.3 J/(mol·K).

Formulas (12)—(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, we then obtained the equation to determine the heat capacity. The experimental values $C_p(T)$ differed from the calculated data by no more than 5 %.

According to the obtained equations of heat capacity and reference data on the heat of formation $T_{ад}$, the calculation is performed in accordance with expression (2). First, the thermal effect is calculated by the formula [12]

$$\Delta H(T_{пл}) = \int_{T_o}^{T_{пл}} C_p(T)dT, \tag{16}$$

and is compared with the value Q. When $\Delta H(T_{пл}) > Q$ adiabatic temperature $T_{ад}$ was lower than the melting point of the product $T_{пл}$ and its value was found from equation (2). If $\Delta H(T_{пл}) < Q$, then $T_{ад} \geq T_{пл}$, and in this case it is necessary to consider melting of the formed product.

The heat of fusion of intermetallics is estimated by the formula [17]

$$\Delta H_{ф.п.} = \Delta S_{ф.п.} \cdot T_{пл}, \tag{17}$$

since it is known that the melting entropy of inorganic compounds can be estimated in the range of 5…7 cal/mol·deg (20.9… .29.3 J/mol·K). The heat capacity of the liquid product $C_{ж}$ was assumed to be $8 \cdot n$ cal/mol·deg, where n — is the number of atoms in the molecule of the compound formed. The adiabatic combustion temperatures of binary metal systems that form various intermetallic compounds. Thermodynamic analysis showed that for most metal systems the adiabatic combustion temperature is equal to or higher than the melting point of the final product — the intermetallic compound. This condition is sufficient for the self-propagating high-temperature synthesis to take place under normal conditions.

Therefore, thermodynamic analysis of thermochemical reactions of intermetallic formation by the ratio of adiabatic combustion temperature and melting point of the formed product showed that the studied reactions can be divided into two groups. The first group includes systems in which the adiabatic combustion temperature is lower than the melting point of the compound formed ($T_{ад} < T_{пл}$).

First of all, it is the Ti + Al system, in which synthesis under normal conditions is unlikely. Preheating is required to carry out the synthesis reaction. The second group includes systems for which the adiabatic combustion temperature is equal to or exceeds the melting point of the product formed ($T_{ад} \geq T_{пл}$).This group includes the Ni + Al system, which, as shown by the thermodynamic calculation of the maximum adiabatic temperature, is characterized by the interaction in the combustion mode under normal conditions (T_0 = 298 K).

Thermodynamic calculations of the stability of intermetallic compounds, as well as other chemical compounds, based on the use of the Gibbs-Helmholtz equations, as the dependence of the change in free Gibbs energy on temperature [5]

$$\Delta G_T = \Delta H_T^{\circ} - T \cdot \Delta S_T^{\circ}, \tag{18}$$

where ΔG_T — free Gibbs energy, kJ/mol; ΔH_T° — enthalpy of formation, kJ/mol; ΔS_T° — entropy, J/mol·K; T — temperature, K.

In the case of the reaction of intermetallic in the Me-Al system according to the equation

$$Me_x + Al_y = Me_xAl_y, \tag{19}$$

the standard enthalpy of formation and entropy of this chemical reaction is calculated as follows [5]:

$$\Delta H_{298}^{\circ} = \nu_1 \sum \Delta H_{298\,прод}^{\circ} - \nu_2 \sum \Delta H_{298\,исх}^{\circ}; \tag{20}$$

$$\Delta S_{298}^{\circ} = \nu_1 \sum \Delta S_{298\,прод}^{\circ} - \nu_2 \sum \Delta S_{298\,исх}^{\circ}, \tag{21}$$

where $\sum \Delta H_{298\,прод}^{\circ}$ — sum of standard enthalpies of formation of reaction products, kJ/mol; $\sum \Delta H_{298\,исх}^{\circ}$ — sum of standard enthalpies of initial substances, kJ/mol; $\sum \Delta S_{298\,прод}^{\circ}$ — sum of standard entropies of reaction products, kJ/mol; $\sum \Delta S_{298\,исх}^{\circ}$ — sum of standard entropies of initial substances, kJ/mol; ν_1 i ν_2 — stoichiometric coefficients.

Next, the Gibbs energy at standard temperature is calculated for the reactions of formation of compounds Me_xAl_y according to formula (19).

Next, the Kirchhoff equation calculates the change in enthalpy and entropy of intermetallics at the required temperature T [12]

$$\Delta H_T = \Delta H_{298}^{\circ} + \int_{298}^{T} \Delta C_p dT; \tag{22}$$

$$\Delta S_T = \Delta S_{298}^{\circ} + \int_{298}^{T} \frac{\Delta C_p dT}{T}, \tag{23}$$

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 intermetallic at temperature T

$$\Delta G_T = \Delta H_T - T \cdot \Delta S_T. \tag{24}$$

Enthalpy calculations showed that in the temperature range 298… $T_{пл}$, K the thermal effects of these chemical reactions have values < 0 and, accordingly, the reactions occur with the release of heat.

Analyzing the dependence of the free Gibbs energy on temperature, we can conclude that the stability of intermetallic compounds formed in the *Ti-Al* and *Ni-Al*. systems. Each compound of the system is characterized by a negative value of Gibbs energy. Estimation of the change in Gibbs free energy ΔG_T during the formation of various aluminides with aluminum and Nickel showed that the intermetallic phase $NiAl_3$. It is slightly lower ΔG in the metastable phase of Ni_2Al_3, but it can be formed only after a few intermediate transformation reactions, which is thermodynamically unlikely.

Calculations of the change in the Gibbs free energy ΔG during the formation of various aluminum and titanium aluminides confirmed that the $TiAl_3$ phase has the lowest energy of stable intermetallics in the entire temperature range. Slightly lower ΔG in metastable phases $TiAl_2$ and Ti_2Al_5, but they can be formed only after a few 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 components involved in these reactions, the equilibrium constants of all independent reactions possible in these systems were determined. The equilibrium constant is associated with a change in the Gibbs energy of the reaction through the relationship [3, 5]

$$\Delta G_T^o = -RT\ln k\,; \tag{25}$$

$$k_T = exp\left(-\frac{\Delta G_T^o}{RT}\right). \tag{26}$$

Equations (25) and (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 from the experimentally found value of the equilibrium constant. The results of calculating the rate constant of the reaction rate of formation of intermetallic compounds in Ni-Al and Ti-Al systems show that with increasing temperature the value of the constant decreases, ie heat is released as a result of reactions (thermochemical exothermic reaction $Q > 0$).

Based on the thermodynamic calculation, it is established that the reaction of formation of intermetallic compounds proceeds in the forward direction, at all possible temperatures of the process. Large values of the equilibrium constant (for $NiAl$ — $k = 5{,}03\cdot10^{18}$, $TiAl$ — $k = 2{,}3\cdot10^{11}$) show that under standard equilibrium conditions the reaction is very shifted to the right, which means that at 298 K a stable compound of intermetallics is formed . At low temperatures, less than 933 K, the reaction proceeds very intensely, as evidenced by the very high value of the reaction constant.

The activation energy of each reaction can be estimated by the formula [27]

$$E_a = \frac{R[ln\,k_2 - ln\,k_1]}{\frac{1}{T_1} - \frac{1}{T_2}}. \tag{27}$$

We find the value of the reaction rate constant of the formation of intermetallic compounds at temperatures $T_1 = 298$ K i $T_2 = 1000$ K. Accordingly, we obtain for the Ni-Al − $\ln k_1 = 16{,}05$ i $\ln k_2 = 3{,}21$; for the system Ti-Al $\ln k_1 = 26{,}89$ i $\ln k_2 = 3{,}57$. The values of the activation energy of the intermetallic alloy formation reaction obtained by thermodynamic calculation were 45.153 kJ/mol and 82.263 kJ/mol, respectively.

Therefore, based on thermodynamic analysis of intermetallic alloys formation reactions under thermochemical pressing conditions, the equilibrium constants of all independent intermetallic formation reactions in Ni-Al and Ti-Al systems and their activation energies are obtained. It was found that the activation energy for the reaction 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 thus show the complexity of the SHS reaction under normal conditions. To carry out the synthesis reaction in the Ti-Al system requires preheating the system to a temperature of 400…600 K.

The second most important problem 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 required to obtain the desired product. Such thermodynamic analysis is especially important in complex multicomponent systems, when the composition of combustion products is not obvious due to the presence of competitive side effects, phase transformations, dissociation. Thermodynamic calculations of the change in Gibbs free energy ΔG in the formation of various aluminum and titanium aluminides confirmed that in the entire temperature range the lowest energy of stable intermetallics has the phase $TiAl_3$.

Thermodynamic calculations of the equilibrium state in the Ni-Al system have shown that intermetallics are always synthesized into a single-phase product of the specified stoichiometry. In the NiAl formation system, the monophase product is NiAl Nickel monoaluminide. In the TiAl system, the calculation showed that although the target reaction product here is titanium monoaluminide TiAl, the main (inevitably present) by-product is the Ti3Al phase. The ratio of phase components (TiAl to Ti3Al) is 70: 30 %, which is in good agreement with the available results of the study of structural and phase formation of alloys obtained by thermochemical pressing of powder mixtures of Ni-Al and Ti-Al [13—15].

Therefore, the optimal areas for obtaining certain phases, determined thermodynamically (calculation), will monitor the processes of both phase formation and formation of the microstructure of the product at all stages of the process, identify the sequence of phase and structural transformations and mechanisms of interaction of these metals with aluminum in high temperature synthesis.

Conclusions

Thus, thermodynamic analysis of intermetallic systems and determination of adiabatic temperatures of formation of various compounds leads us to believe that the implementation of the process of thermochemical pressing is not the only exception, but the rule for many refractory compounds. Almost every refractory intermetallic compound of metals resistant to high temperatures is formed from elements with strong heat release, and can be obtained by thermochemical pressing. It should also be noted that despite the short duration of the thermochemical pressing process, the obtained products are close in composition to thermodynamic equilibrium.

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МОДЕЛЮВАННЯ І ТЕРМОДИНАМІЧНИЙ АНАЛІЗ РЕАКЦІЙ ПРИ ТЕРМОХІМІЧНОМУ ПРЕСУВАННІ ПОРОШКІВ ІНТЕРМЕТАЛІДНИХ СПЛАВІВ

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Реферат

Представлено результати термодинамічного аналізу реакцій, що можливі під час одержання порошкових інтерметалідних сплавів за умов термохімічного пресування. На основі термодинамічного аналізу перебігу реакцій утворення інтерметалідних сплавів в умовах термохімічного пресування отримані термодинамічні властивості та константи рівноваги всіх незалежних реакцій утворення інтерметалідів у системах Ni-Al і Ti-Al та їхні енергії активації. Встановлено, що для реакції взаємодії титану та алюмінію з утворенням інтерметалідів енергія активації становить 82,263 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 термохімічних реакції в звичайних умовах. Аналіз рівноважного стану інтерметалідних сплавів NiAl та TiAl показав, що механізми структуроутворення сплаву якісно розрізняються. На відміну від синтезу алюмініду нікелю, який маж монофазний продукт, дифузійні процеси в TiAl відбуваються повільніше, і синтез г-фази відбувається в процесі охолодження, з повільним рухом межі розділу та зі слабким тепловиділенням (повторне структуроутворення). Рівноважний склад продукту синтезу у системі Ti-Al хоча і цільовим продуктом реакції тут є моноалюмінід титану г-TiAl, але основним (неминуче присутнім) побічним продуктом є б$_2$-Ti$_3$Al.

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