UDC 544.3:669.71

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THERMODYNAMICS ANALYSIS OF FLOWING FOR SHS-REACTIONS IN SYSTEM «TITANIUM-ALUMINIUM»

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The work is devoted to the thermodynamic analysis of the reactions that are possible at the preparation of intermetallic titanium-aluminum alloys in conditions of self-propagating high-temperature synthesis (SHS). Thermodynamic analysis showed that for titanium-aluminum system adiabatic combustion temperature is below the melting point of the final product - the intermetallic compound, which is a sufficient condition for the occurrence of SHS-reaction at normal conditions. To carry out the synthesis reaction there is required coarse heating of system to temperature 400-600 K. Also, on base of thermodynamic analysis, there is established sequence of SHS-reactions leading to the formation of γ-*TiAl* alloys that contributes to the elucidation of the mechanism of the process.

Keywords: thermodynamic analysis, intermetallic compounds, SHS-reaction, titanium-aluminum alloy

Development of new materials with the improved physical-mechanical parameters for work at extreme conditions is actual for aviation industry. It is known that large attention gets to the alloys on intermetallic basis of the system *Ti-Al* [1]. Therefore a greater value is acquired realization of thermodynamics analysis of reactions of formation of the noted alloys and determination of maximal adiabatic temperatures of process and thermodynamics properties.

The temperatures of SHS-processes expect at supposition of adiabaticity, id est. to absence of heat losses from the area of reaction, for the case of complete transformation of reagents on eventual products. Thus equality of enthalpy of initial matters must be executed at a settemperature T_0 and temperature of eventual products T_{ad} [2]:

$$\sum_{i=1}^{n}\left[H\ T_{ad}\ - H\ T_0\ \right]_i = \Delta H = Q_x\ , \qquad (1)$$

where T_{ad}, T_0 – adiabatic and initial temperatures of reactions, respectively; Q_x – a heat effect of reaction. Data summarize in relation to all products of reactions.

Most complications during a thermodynamics analysis arise up in connection with unstudiedness of temperature dependence of heat capacity of connections which appear. For determination of coefficients of formula $C_p\ T\ = a_0 + a_1 \cdot 10^{-3} T + a_2 \cdot 10^5 T^{-2}$, used equation of Tsagareshvili and Gvelisiani [3]

$$a = \frac{a_0}{n} = \left(5{,}95 - \frac{0{,}3 C_{p298}^{at} \cdot \theta}{T_{i\ddot{e}}} \right)\ ;\quad b = \frac{a_1}{n} = \frac{0{,}34 C_{p298}^{at}}{T_{i\ddot{e}}}\ ;\quad \tilde{n} = \frac{a_2}{n} = 0{,}9\ a + b \cdot 298 - C_{p298}^{at}\ \cdot 10^5\ , \qquad (2)$$

where $\tilde{N}_{\delta 298}^{at}$ – a standard gram-atomic heat capacity; n – an quantity of atoms in connection; θ – is a characteristic temperature.

The temperatures of melting and polymorphic transformations determined from the diagram of the state. The absent values of entropy of intermetallides, that appear, expected on the formula of Eastman:

$$S_{298}^{0} = R \cdot \left(1{,}5 \ln A_{mid} + \ln V_{mid} - 1{,}5 \ln T_{mel} + a\right), \quad (9)$$

where A_{mid} – molecular mass of connection which is attributed to the atoms in him; V_{mid} – a middle atomic volume; T_{mel} – an absolute temperature of melting of connection; a – constant, a = 52.3 Joules/(mole·K).

A thermodynamics analysis showed that for most intermetallic phases of the system «*Ti-Al*» adiabatic temperature of burning below of temperature of melting of the finished product. Therefore a necessity is the previous heating in the system *Ti-Al* to the temperature 400-600 K.

The calculations of Gibbs energy formation enthalpy for intermetallides in a wide temperature interval carried out with the use of classic equation the isotherms of Vant-Goff and reference data in relation to the standard sizes of formation enthalpy, entropy, temperature rows of heat capacity, and also temperature and heat effects of phase transitions.

At flowing of reaction of intermetallides formation in the system «metal - aluminium» on equation:

$$Me_x + Al_y = Me_x Al_y, \quad (12)$$

standard enthalpy of formation and entropy of this chemical reaction is expected on formulas:

$$\Delta H_{298}^{0} = \nu_1 \cdot \sum \Delta H_{298\ pro}^{0} - \nu_2 \cdot \sum \Delta H_{298\ ini}^{0}; \quad (13)$$

$$\Delta S_{298}^{0} = \nu_2 \cdot \sum \Delta S_{298\ pro}^{0} - \nu_2 \cdot \sum \Delta S_{298\ ini}^{0}, \quad (14)$$

where ν_1, ν_2 – stoichiometrical coefficients of reaction products and initial matters.

With the use of Kirchhoff equation there are calculated treason of enthalpy and entropy of intermetallides at a necessary temperature T:

$$\Delta H_T = \Delta H_{298}^{0} + \int_{298}^{T} \Delta C_p \, dT; \quad (15)$$

$$\Delta S_T = \Delta S_{298}^{0} + \int_{298}^{T} \frac{\Delta C_p \, dT}{T}, \quad (16)$$

where ΔC_p – treason of heat capacity depending on a temperature, Joules/(mole·K).

For some connections calculations executed with the use of the program «TERRA» [10].

The calculations of enthalpy showed that in the interval of temperatures 298-T_{mel} the heat effects of the considered chemical reactions have value $\Delta G_T < 0$ and according reaction take place with release of heat. Every connection of the system is characterized by the negative value of Gibbs energy. The estimation of treason of free Gibbs energy ΔG_T during formation of different aluminides from an aluminium and titan showed that in all temperature range the phase $TiAl_3$ has the least energy from stable intermetallides. A few more subzero value ΔG_T can be in the metastable phases Ti_5Al_3, Ti_9Al_{23} and Ti_5Al_{11}, but such phases can be formed only through a few intermediate reactions of transformation, that thermodynamics small probably.

Conclusions. Researches of thermodynamics properties during the making of intermetallic titanium-aluminium alloys at the conditions of self-propagating high temperature synthesis, allowed to assume the next sequence of formation of intermetallic connections $TiAl_3 \Rightarrow Ti_3Al \Rightarrow TiAl$.

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