UDC 544.3:669.71

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

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The article is devoted to the thermodynamic analysis of the reactions that are possible at the preparation of intermetallic nickel-aluminum alloys in self-propagating high-temperature synthesis (SHS). Thermodynamic analysis showed that for nickel-aluminum system adiabatic combustion temperature is at the melting point of the final product - the intermetallic compound, which is a sufficient condition for the occurrence of SHS-reaction at normal conditions. Also, on base of thermodynamic analysis, the established sequence of SHS-reactions leading to the formation of nickel-aluminum alloys, which contributes to the elucidation of the mechanism of the process.
Keywords: thermodynamic analysis, intermetallic compound, SHS-reaction, nickel-aluminum alloy

Entry. At the estimation of for making possibilities of different inorganic connections, in particular intermetalediв, the method of self-propagating high temperature synthesis (SHS) all greater value a thermodynamics analysis acquires, first of all determination of maximal adiabatic temperatures for process and thermodynamics properties.

This work is sacred to the thermodynamics analysis of reactions which are possible at the making of intermetaled nickel-aluminium alloys at the conditions of SHS, examining this procedure as method for the evaluation of the most reliable chemical transformations, which assists clearing-up of mechanism for flowing and formation of intermetaledних alloys.

From the aluminides of nickel most interest is presented by a phase β-*NiAl*. The noted phase has the best combination of heat-tolerance and mechanical properties, and also characterized by the considerable area of homogenity, that allows in wide limits to vary composition of intermetaled alloy and can be chosen as basis for nickel-aluminium alloys.

For clearing-up of mechanism of formation of nickel-aluminium alloys at the conditions of SHS it follows to calculate the adiabatic temperature for reactions of intermetaled connections formation and them thermodynamics properties.

Atr the calculations of adiabatic temperature of burning it is necessary to know the standard values of warmth for formation of connections ΔH_{298}, temperature dependences of their heat capacity $C_p\ T$ and also warmth of melting L.

Most complications arise on account of unstudiedness of temperature dependences of heat capacity of connections which appear. A warmth over of formation of far for these connections is brought in certificate literature.

A thermodynamics analysis showed that for most intermetaled phases of the system «nickel-aluminium» the adiabatic temperature of burning equals the temperature of melting of the finished product - intermetaled connection. This condition is sufficient for flowing in the system sHS at ordinary conditions.

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

The thermodynamics calculations of firmness of intermetaledних connections, as well as other compounds, are based on the use of equations of Gibbs-Helmholtz, which characterize dependence of charge to free energy of Gibbs on a temperature:

$$\Delta G_T = \Delta H_T^0 - T \cdot \Delta S_T^0 \ , \qquad (7)$$

where ΔG_T - free energy of Gibbs, kJou/mole; T - a temperature, K; ΔH_T^0 - enthalpy of formation, kJou/moleь; ΔS_T^0 - entropy, Jou/(mole·K).

In the case of flowing in the system $Me - Al$ intermetaled formation reaction on equation:

$$Me_x + Al_y = Me_x Al_y \, , \qquad (8)$$

standard enthalpy of formation and entropy of this chemical reaction settles accounts thus:

$$\Delta H_{298}^0 = \nu_1 \cdot \sum \Delta H_{298\ \text{ïðîä}}^0 - \nu_2 \cdot \sum \Delta H_{298\ \text{âèõ}}^0 \ ; \qquad (9)$$

$$\Delta S_{298}^0 = \nu_1 \cdot \sum \Delta S_{298\ \text{ïðîä}}^0 - \nu_2 \cdot \sum \Delta S_{298\ \text{âèõ}}^0 \, , \qquad (10)$$

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

For the formation connection reactions of $Me_x Al_y$ on a formula (8) expected energy of Gibbs at a standard temperature.

With the use of Kirgoff equation changes of enthalpy and entropy of intermetaleds settled accounts at a necessary temperature T:

$$\Delta H_T = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_p \, dT \ ; \qquad (11)$$

$$\Delta S_T = \Delta S_{298}^0 + \int_{298}^{T} \frac{\Delta C_p \, dT}{T} \ , \qquad (12)$$

where $\Delta \tilde{N}_p$ - change of heat capacity depending on a temperature, Jou/(mole·K).

Expected change of Gibbs energy (ΔG_T) of this intermetaled the next stage for temperatures T:

$$\Delta G_T = \Delta H_T - T \cdot \Delta S_T \ . \qquad (13)$$

Calculations executed in a wide interval of temperatures. A settemperature for calculations is choose a standard temperature 298 K, and eventual - maximal

temperature of melting of intermetaled ($T_{i\ddot{e}}$). For some connections calculations executed with the use of the program «TERRA».

The conducted calculations of change of free energy of Gibbs ΔG_T showed during formation of different aluminides, that in all temperature range the least energy from stable intermetaleds is owned by the phase of $NiAl_3$.

Thus, research of thermodynamics properties at the making for intermetaled of nickel-aluminium alloys at the conditions of SHS, allowed to assume the next sequence of reactions :

$$Ni + 3Al \Rightarrow NiAl_3 \ ; \tag{14}$$

$$Ni + NiAl_3 \Rightarrow Ni_2Al_3 \ ; \tag{15}$$

$$Ni + Ni_2Al_3 \Rightarrow 3NiAl \ . \tag{16}$$

Conclusions. A thermodynamics analysis showed that for the system *Ni-Al* the adiabatic temperature of burning equals the temperature of melting of the finished product is intermetaled connection which is a sufficient condition for flowing of SHS-reaction at ordinary conditions. Also, on the basis of thermodynamics analysis, is set sequence flowing of SHS-reactions, which conduce to creation of nickel-aluminium alloys, which assists clearing-up of process mechanism of their formation.