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B. Sereda[1], Doctor of Technical Sciences, Professor, seredabp@ukr.net
B. Hina[2], Doctor of Physical and Mathematical Sciences, Professor, Chief Researcher
D. Sereda[1], Candidat of Technical Sciences, Associate Professor
[1]Dniprovsk State Technical University, Kam'yanske
[2]Physics and Technology Institute of the National Academy of Sciences of Belarus, Minsk

THERMODYNAMIC CHARACTERISTICS OF SUPERSATURATED SOLID SOLUTIONS IN THE Ni–Al SYSTEM: COMPARISON OF DIFFERENT APPROACHES

Thermodynamic characteristics (the formation enthalpy and Gibbs energy) of nickel- and aluminum-base supersaturated solid solutions in binary system Ni-Al are estimated using the semi-empirical Miedema model and the CALPHAD approach. The comparison of these two approaches is made and the limitations of the Miedema model are revealed.

***Keywords**: Ni-Al system; supersaturated solid solution; thermodynamic properties; formation enthalpy; Miedema model; CALPHAD approach.*

Термодинамічні характеристики (ентальпія утворення та енергія Гіббса) перенасичених твердих розчинів на основі нікелю та алюмінію в бінарній системі Ni-Al оцінені за допомогою напівемпіричної моделі Міедеми та підходу CALPHAD. Проведено порівняння цих двох підходів та виявлено обмеження моделі Miedema.

***Ключові слова**: система Ni-Al; перенасичений твердий розчин; термодинамічні властивості; ентальпія утворення; модель Міедеми; підхід CALPHAD.*

Problem's Formulation

Supersaturated solid solutions are formed in many binary and multicomponent systems during mechanical alloying (MA) — intensive grinding of a mixture of powders in a highly loaded grinding device, for example, a vibration or planetary mill, attritor, etc. [1—3]. In MA, as a result of collisions of the “ball-particle-ball” or “ball-particle-wall” type, the initial particles of pure components are destroyed and cold welding along the formed juvenile surfaces occurs, with the formation of composite (most often layered) particles. In the course of further intense periodic plastic deformation of such composite particles, in which the characteristic layer size is 0.1—0.5 μm, accelerated diffusion of components and metastable phase transitions occur. This leads to the formation of nonequilibrium phase and structural states, such as nanostructures, supersaturated solid solutions, amorphous and quasicrystalline phases.

It is also known that mechanical activation of powder components in similar devices is used to influence the processes of self-propagating high-temperature synthesis (SHS). This process is called mechanically activated SHS (MA-SHS) [5—8]. In this case, a decrease in the ignition and combustion temperatures, a change in the speed of the SHS wave, and a significant decrease in the effective activation energy of the process are observed. Moreover, during SHS in a Ni + Al powder mixture subjected to preliminary mechanical activation by intense short-term (up to 4.5 min) grinding in a planetary mill with centrifugal acceleration of balls up to 60 g, a new phenomenon was discovered — purely solid-phase combustion, when the interaction temperature was found to be below the melting point of the most low-melting component — aluminum (Tm (Al) = 660 °C) [9, 10].

In this regard, it should be noted that the process of mechanoactivation of the powder charge can be considered as the initial stage of mechanoalloying. The Ma duration is ~ 1—10 h, and its purpose is to obtain powder materials with a metastable phase and / or structural state [1—3]. In contrast to ML, the purpose of mechanical activation as a preliminary stage of MA-SHS is to grind reagent particles and increase the contact area between them. Grinding is usually stopped when the composite particles are formed and lasts several minutes. At the same time, as noted in a number of works, the effects observed during MA-SHS can be associated with the formation of metastable phase and structural states at the boundaries of component interlayers in composite particles, i.e. at the nanoscale [11].

Formulation of the study purpose

To assess the physical mechanism of MA effect on the subsequent SHS, it is necessary, first of all, to evaluate the thermodynamic characteristics (enthalpy and Gibbs energy) of supersaturated solid solutions based on pure metals. Carrying out such studies is associated with significant experimental difficulties.

In this regard, the purpose of this work is to theoretically estimate the thermodynamic characteristics of supersaturated solid solutions in the Ni-Al system, in which a strong effect of mechanical activation on SHS was observed [9—11], and to compare the results obtained using different approaches.

Presenting main material

At present, the following approach is used to describe the thermodynamic characteristics of multicomponent condensed phases (melts, substitutional solid solutions, and compounds) with a certain homogeneity region [12]. All phases, even the so-called "linear" compounds, which do not have a visible region of homogeneity on the phase diagram and are depicted as a vertical straight line, are considered as solutions, and their thermodynamic parameters (Gibbs energy G, enthalpy H and entropy S) are not determined by formula unit (for example,TiB_2), and for 1 mol of solution (in this example, for the formula $Ti_{0.33}B_{0.67}$). The expressions for the Gibbs energy and phase enthalpy φ are as follows:

$$G_\varphi = \sum_{i=1}^{k} x_i G_i^\varphi + H_{ex}^\varphi - TS_{id}, \tag{1}$$

$$H_\varphi = \sum_{i=1}^{k} x_i H_i^\varphi + H_{ex}^\varphi, \tag{2}$$

$$S_{id} = -R\sum_{i=1}^{k} x_i \ln x_i, \tag{3}$$

$$G_i^\varphi = H_i^\varphi - TS_i^\varphi. \tag{4}$$

Here G_i^φ, H_i^φ and S_i^φ — are the Gibbs energy, enthalpy and entropy of the pure component i in the phase state φ, H_{ex}^φ — is the excess enthalpy of mixing associated with the chemical interaction of atoms, S_{id} — is the ideal (i.e. configurational) arrangement of atoms of different types, x_i — is the atomic concentration of the ith component, R — is the universal gas constant, T — is the temperature, k — is the number of components.

The quantities G_i^φ and H_i^φ , included in formulas (1), (2) and (4), are defined as polynomials

$$G_i^\varphi = a_i + b_i T + c_i T \ln T + \sum_n d_{i,n} T^n + H_i^{SER} + G_{i,pres}^\varphi + G_{i,mag}^\varphi, \tag{5}$$

$$H_i^\varphi = a_i - c_i T - \sum_n (n-1) d_{i,n} T^n + H_i^{SER} + H_{i,pres}^\varphi + H_{i,mag}^\varphi, \tag{6}$$

where $G_{i,pres}^\varphi$, $H_{i,pres}^\varphi$ and $G_{i,mag}^\varphi$, $H_{i,mag}^\varphi$ are quantities describing the contributions of pressure and magnetic ordering to the Gibbs energy and enthalpy of the ith element in the phase state φ, H_i^{SER} is the standard value (Standard Element Reference), a_i, b_i, c_i and $\underline{d_{i,n}}$ — are the numerical parameters for of the i-th element, n — is an integer. The value H_i^{SER} = $H_i(T=298) - H_i(T=0)$ is small and it makes sense to correct when passing from T=298 K to T=0 K as to the standard reference temperature for thermodynamic quantities G and H.

All parameters included in formulas (5) and (6) are given in the SGTE (Scientific Group Thermodata Europe) thermodynamic database [13] for all metallic and non-metallic elements (except gases) in various phase states — as in liquid, and in a solid with different crystal lattices. It also contains calculated data for hypothetical phase states of solid elements, i.e. states with such a crystal lattice, which for a given element does not exist in a free form in nature. These values are used for situations where the type of crystal lattice in which a given element is located as a solute differs from its own lattice in equilibrium.

The main problem in calculating the thermodynamic characteristics of stable and metastable phases is to determine the excess enthalpy of mixing H_{ex}^{φ}. For this, various approaches are used.

Assessment of thermodynamic characteristics of phases according to the Miedema model

The semiempirical Miedema model is used to estimate the enthalpy of formation of compounds (for example, multicomponent intermetallics, carbides, etc.) for which there are no data in the reference literature, as well as for metastable phases, primarily amorphous [14]. It is also used to predict the range of compositions of the liquid phase in the phase diagram, where it is possible to obtain amorphous alloys [15, 16].

According to this approach, the change in enthalpy during the formation of phase φ from components in a given phase state, i.e. in fact, the excess enthalpy of mixing H_{ex}^{φ}, is defined as

$$H_{ex}^{\varphi} = \Delta H^{chem} + \Delta H^{el}, \tag{7}$$

where ΔH^{chem} — is the enthalpy of the chemical, and ΔH^{el} — is the elastic interaction of atoms, the latter being taken into account only for solid crystalline phases.

In the Miedema model, the quantity ΔH^{chem} for the multicomponent phase is calculated as

$$\Delta H^{chem} = \sum_{j>i=1}^{k} x_i x_j \left(x_j^s \Delta H_{i\,in\,j}^{chem} + x_i^s \Delta H_{j\,in\,i}^{chem} \right) f_{ij}, \tag{8}$$

where x_i — is the molar concentration of the ith component, x^s_i — is the concentration of atoms of the ith sort at the boundary of Wigner-Seitz, $\Delta H_{i\,in\,j}^{chem}$ — is the enthalpy of dissolution of element i in j, $i \neq j$, k — s the number of components, f_{ij} — is the parameter , depending on the type of phase.

The quantity x^s_i has the meaning of the fraction of the surface of atoms i, which is in contact with atoms j, $i \neq j$, and for each pair i–j it is determined by the formula:

$$x_i^s = x_i V_i^{2/3} \Big/ \left(x_i V_i^{2/3} + x_j V_j^{2/3} \right), \quad x_j^s = 1 - x_i^s, \tag{9}$$

where V_i — is the molar volume of the i-th element, the values of which for some substances are corrected taking into account the type of the crystal lattice [17].

The parameter f_{ij}, $i \neq j$, has the form

$$f_{ij} = 1 + \gamma \left(x_i^s + x_j^s \right)^2, \tag{10}$$

where γ=5 for the amorphous phase, 0 for disordered solid solutions and 8 for ordered phases (solid solutions and intermetallic compounds) [18].

The values $\Delta H_{i\,in\,j}^{chem}$ are determined in the following form [11, 14]:

$$\Delta H_{i\,in\,j}^{chem} = \frac{2 P_{ij} V_i^{2/3}}{n_i^{-1/3} + n_j^{-1/3}} \left[-\left(\varphi_i^* - \varphi_j^* \right)^2 e + \frac{Q}{P_{ij}} \left(n_i^{1/3} - n_j^{1/3} \right)^2 - \frac{R}{P_{ij}} \right]. \tag{11}$$

Here e — is the elementary electric charge (electron charge), φ_i^* — s the electronegativity parameter for the i-th component, n_i — is the electron density parameter at the Wigner-Seitz, P_{ij} and R/P_{ij} — are numerical parameters depending on the nature of the i–j, the value Q/P_{ij} = 9,4 for all substances. For the Ni-Al: P_{ij} =0,128, R/P_{ij} = 1,9, and the values of the remaining parameters for nickel and aluminum included in formula (11) are given in tabl. 1.

Miedema's model uses specific dimensions of quantities, which here, as in the original [14, 17], are given in English notation: $[V_i]$=cm^3, $[R/P_{ij}]$=V^{2}e, $[n_i]$=d.u., $[\varphi_i$*]=V, $[Q/P_{ij}]$=V^{2}e(d.u.)$^{-2/3}$, $[P_{ij}]$= V^{-1}cm^{-2}(d.u.)$^{-1/3}$, where V≡ Volt, e — electron charge, cm≡см, d.u. (density unit) — unit of electron density: 1 d.u. ≈ $6 \cdot 10^{22}$ cm^{-3} [14]. From such a definition of dimensions, it becomes clear that in formula (5) the factor e with the term $(\varphi^*_i - \varphi^*_j)^2$ is written only to maintain the balance of dimensions, i.e. here e=1, and not a physical quantity, which is $1{,}602 \cdot 10^{-19}$ Кл.

Table 1. Parameters of the Miedema model with corresponding dimensions for Ni and Al [17, 20]

	φ_i^*, V	$n_i^{1/3}$, (d.u.)$^{1/3}$	$V_i^{2/3}$, cm^2	Hooke's module μ, GPa	Compressibility ζ, GPa^{-1}
Ni	5,20	1,75	3,52	26,2	$1{,}385\cdot10^{-2}$
Al	4,2	1,39	4,64	76,0	$0{,}538\cdot10^{-2}$

The quantity $\Delta H^{chem}_{i\,in\,j}$ has the dimension eV (electron volt) per 1 atom, and a conversion factor is used to convert to J/mol: 1 J/mol = $1{,}6021\cdot10^{-19}\cdot N_A$ eV = $96{,}494\cdot10^3$ eV, where $N_A = 6{,}023\cdot10^{23}$ mol $^{-1}$ – Avogadro's number.

The term ΔH^{el} in expression (7), which takes into account the contribution of the elastic interaction of atoms, is determined similarly to the chemical energy in formula (8) [19, 20]:

$$\Delta H^{el} = \sum_{j>i=1}^{k} x_i x_j \left(x_j^s \Delta H^{el}_{i\,in\,j} + x_i^s \Delta H^{el}_{j\,in\,i} \right) f_{ij}\,, \tag{12}$$

where $\Delta H^{el}_{i\,in\,j}$ — is the enthalpy of elastic interaction of atoms for the solution of element i in j, $i \neq j$.

It is convenient to $\Delta H^{el}_{i\,in\,j}$ write expressions for for a pair of atoms A-B, i.e. putting $i \equiv A$ for the dissolved element (solute) and $j \equiv B$ for the solvent [19, 20]:

$$\Delta H^{el}_{A\,in\,B} = \frac{2\mu_B (W_B - W_A)^2}{3W_B + 4\mu_B \zeta_A W_A}\,, \tag{13}$$

where μ_B — is Hooke's modulus of solvent B, ζ_A — s the compressibility of the dissolved component A, $\zeta_A = K_A^{-1}$, where K_A is the modulus of uniform compression, W_A and W_B — are the corrected molar volumes of the components for the solid solution.

The values of μ and ζ for Ni and Al are given in table. 1. The values W_A and W_B, included in (13) are calculated by the following expressions [19]:

$$W_A = V_A + \alpha_{A\,in\,B} \frac{\varphi_B^* - \varphi_A^*}{n_A}\,, \quad W_B = V_B + \alpha_{A\,in\,B} \frac{\varphi_B^* - \varphi_A^*}{n_B}\,, \tag{14}$$

where V_A and V_B — are the molar volume of pure substances A and B, and the coefficient $\alpha_{A\,in\,B}$ is defined as:

$$\alpha_{A\,in\,B} = -P_0 \frac{V_A^{all}}{n_A^{-1/3} + n_B^{-1/3}}\,. \tag{15}$$

Here $P_0 = 1{,}5$ — is an empirical constant with the dimension cm·(d.u.)$^{2/3}$·V^{-1}, and V_A^{all} — is the molar volume of element A in the alloy, which is determined by the formula [21]

$$\left(V_A^{all}\right)^{2/3} = V_A^{2/3}\left[1 + \alpha_A x_B \left(\varphi_A^* - \varphi_B^*\right)\right], \tag{16}$$

where α_A — is an empirical coefficient taking values 0,14, 0,10, 0,07 and 0,04 for elements with valence v = 1, 2, 3 and >3, respectively; e.g. for aluminum $\alpha_{Al} = 0{,}07$, but for nickel $\alpha_{Ni} = 0{,}04$ [17].

Thus, formulas (7)—(16) describe the thermodynamic parameters of the phases per 1 mol of solution in the framework of the semiempirical Miedema model. It should be noted that in many works where the Miedema model is used, elastic energy is not taken into account without explaining the reasons.

To compare the calculation results and estimate the error of the Miedema model, we will use the CALPHAD approach (CALculation of PHAse Diagrams — calculation of phase diagrams) for the same phases — supersaturated solid solutions based on Al and Ni in the Ni-Al binary system.

Calculation of thermodynamic characteristics of phases using the CALPHAD approach

Within the framework of the CALPHAD approach, which was developed for calculating double and multicomponent phase equilibrium diagrams [12], the excess enthalpy of mixing for the binary phase φ is determined using the regular solution model:

$$H^{\varphi}_{ex} = x_1 x_2 L^{\varphi}_{12}\,, \tag{17}$$

where x_1 and x_2=1–x_1 — are the atomic concentrations of the components, and the parameter of pair interaction of atoms L^{φ}_{12} is described by the Redlich-Kister-Muggianu polynomial:

$$L^{\varphi}_{12} = \sum_{n} {}^{n}L^{\varphi}_{12}\left(x_1 - x_2\right)^n, \quad n \geq 0. \tag{18}$$

According to [22], the parameters of polynomial (18) are the same for solid solutions based on Ni and Al, since both of these elements have the same crystal lattice — fcc, and have the following values (in SI units, that is, J / mol):

$$\begin{aligned} {}^{0}L^{fcc}_{12} &= -162407.75 + 16.213T, \quad {}^{1}L^{fcc}_{12} = 73417.8 - 34.914T, \\ {}^{2}L^{fcc}_{12} &= 33471.01 - 9.837T, \quad {}^{3}L^{fcc}_{12} = -30758.01 + 10.253T. \end{aligned} \tag{19}$$

n the CALPHAD approach, it is important to determine the standard state of the components in a given phase — i.e. parametersG_i^{φ}, H_i^{φ}, included in formulas (1) and (2). As noted above, Ni and Al in equilibrium have the same fcc (phase-centered cubic) lattice, but nickel is ferromagnetic and aluminum is paramagnetic. Since to determine the thermodynamic parameters of the components it is necessary to take into account the magnetic ordering (see formulas (5) and (6)), the following are taken as the standard states of the components of two solid solutions (based on Al and based on Ni) [22]:

1) solid solution based on nickel: for Ni — Gibbs energy G^{fcc}_{Ni} and enthalpy H^{fcc}_{Ni} of a pure element, taking into account magnetic orderingfor aluminum, the Gibbs energy G^{fcc}_{Al} and enthalpy H^{fcc}_{Al} of the pure component, i.e. for both substances their equilibrium states are taken;

2) a solid solution based on aluminum: for Al — the Gibbs energy G^{fcc}_{Al} and enthalpy H^{fcc}_{Al} of a pure element in an equilibrium state; for Ni — the Gibbs energy and enthalpy in a hypothetical paramagnetic state with an fcc lattice ($G^{fcc,para}_{Ni}$ и $H^{fcc,para}_{Ni}$), i.e. disregarding magnetic ordering.

The specified parameters for pure components were calculated based on the values given in the SGTE database [13].

Calculations of the Gibbs energy and enthalpy using the CALPHAD model were performed per mole of the two-component phase for two supersaturated fcc solid solutions — one based on aluminum (in the composition range from 0 to 60 at.% Ni) and based on nickel (composition range from 40 to 100 at % Ni) at room temperature T_0=298 K. The results are shown in Fig. 1. It also shows the estimates of these thermodynamic parameters according to the semiempirical model of Miedema in the entire range of concentrations — from 0 to 100 % Ni.

A slight difference in the enthalpy and Gibbs energy of supersaturated solid solutions based on aluminum (dash-dotted black line in Fig. 1, *a,b*) and nickel (dash-dotted gray line in Fig. 1, *a,b*), calculated using CALPHAD- approach, which is noticeable in the range of compositions $0.4 \leq x_N \leq 0.6$, is associated with the fact that different standard states of the components described above were used for their thermodynamic description. This is also the reason that the entropy of the saturated solid solution based on aluminum (black dash-dotted line in Fig. 1,*b*) is slightly higher than for the solution based on nickel (gray dash-dotted line in Fig. 1,*b*) within the CALPHAD approach. Note that, in the calculations using the Miedema model, their equilibrium states were taken as the standard state of the components of the fcc solid solution; therefore, the entropy of the supersaturated solution (black line in Fig. 1*b*) coincides with the values for the fcc solution based on Ni, determined by CALPHAD — models. The ideal entropy of mixing in both models is the same (dotted line in Fig. 1,*b*), since it is determined by formula (3), and its maximum value is small: $max(S_{id})$ = 5,76 J/(mol·K) at x_{Ni}=0,5.

As can be seen from Fig. 1a, within the framework of the Miedema model, the enthalpy of elastic interaction ΔH^{el} (dotted line in Fig. 1, *a*) is comparable with the total fcc enthalpy (fcc) of the Ni-Al solid solution, since the relative differenc $\varepsilon = max|\Delta H^{el}/H_{fcc}| \approx 0{,}24$, i.e. this value makes a significant contribution to the estimation of the enthalpy of formation of the crystalline phase. In this case, in the entire range of concentrations, the enthalpy, estimated using the Miedema model, taking into account the elastic interaction, turns out to be significantly higher (i.e., less negative) than that calculated using the CALPAD approach.

At the same time, as can be seen from Fig. 1, a, the enthalpy of formation of a solid solution without taking into account ΔH^{el} (i.e., only the enthalpy of chemical interaction ΔH^{chem} — see the dotted line in Fig. 1,*a*) is close to the values obtained from CALPAD models. Apparently, this is what motivates the fact that in many cases, when estimating the enthalpy of formation of solid crystalline phases according to the Miedema model, the elastic interaction is not taken into account — as was done, for example, when studying a large number of three-component alloys [23].

The Gibbs energy, estimated by the Miedema model with allowance for the elastic interaction of atoms (solid black line in Fig. 1,*c*), differs significantly from the calculation by the CALPHAD method (dash-dotted lines in Fig. 1,*c*), which is primarily associated with the contribution of the enthalpy component H_{ex}^{φ}. Taking into account only the chemical interaction (values ΔH^{chem}) the free energy of the solution is somewhat closer to the results according to the CALPHAD approach, but in this case the maximum relative deviation is quite large — about 20 % at x_{Ni}=0,6. The data obtained by the CALPHAD method are more reliable, since the Ni-Al phase diagram calculated using this method [22] is in good agreement with the experimental one.

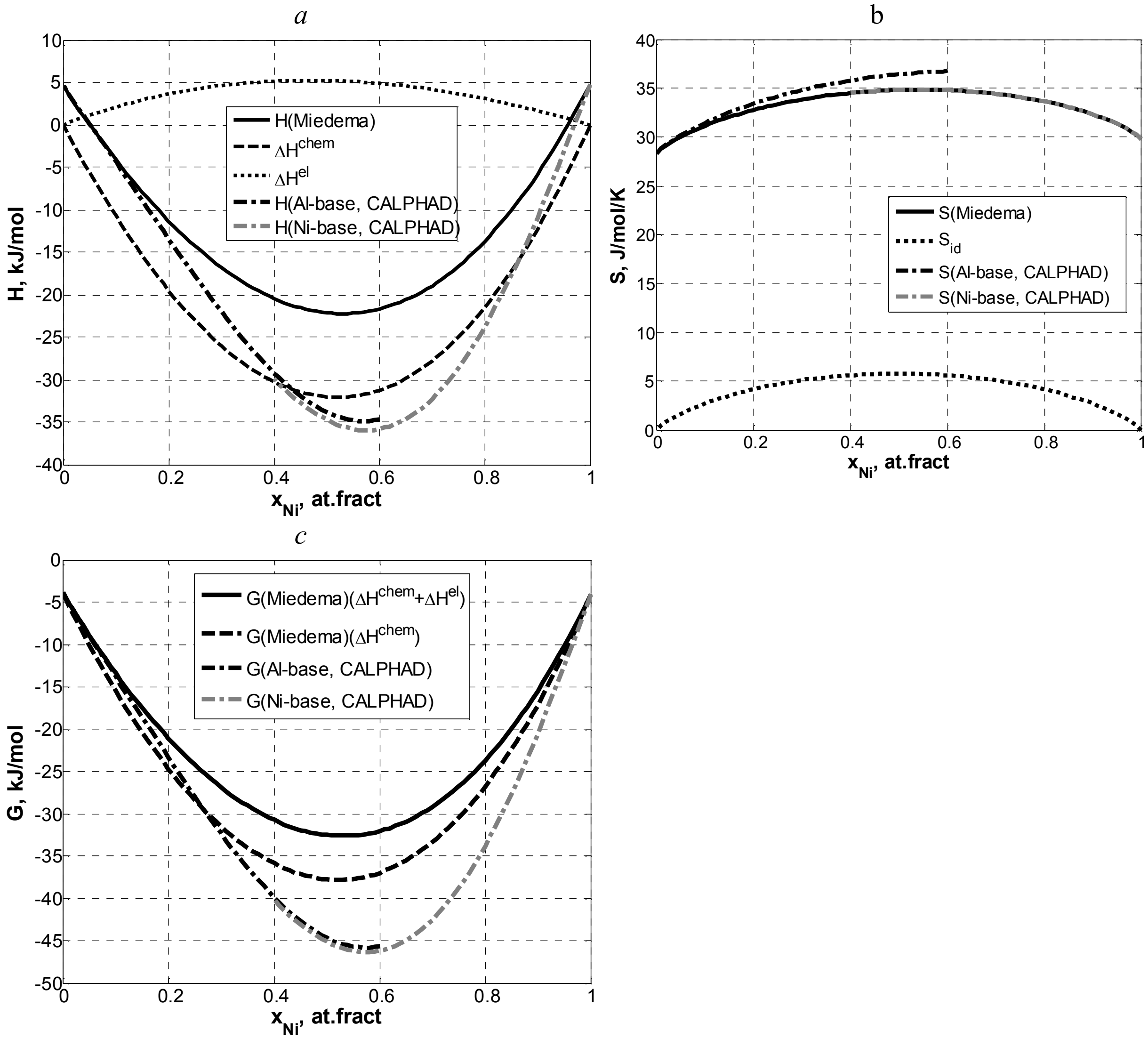

Fig. 1. Thermodynamic characteristics of solid solutions based on nickel and aluminum, calculated using the Miedema model and based on the CALPHAD approach: *a* — enthalpy, *b* — entropy, *c* — Gibbs energy

It should be noted that when calculating the enthalpy of formation of solid three-component alloys according to the Miedema model without taking into account the elastic interaction of atoms, the data [20] were obtained, which significantly differ from the experimental ones. Thus, the relative deviation $\varepsilon = |\Delta H^{chem} – H_{exp}|/H_{exp}$, where H_{exp} — is the experimental value, was 18 % for the Fe-Ni-V, 14 % for the Fe-Ni-Zr system, and about 60 %, for Cu-Ag-Au — from 14 to 82 %, for Au-Sb-Zn — 17—29 %, for Y-Cu-Mg — from 14 to 43 %, for Pb-Sn-Sb — from 29 to 115 %, for Pb-Sn-Zn — 44—57 %, for Cu-Pd-Si alloys — from 24 % to 50 % [20]. Therefore, the calculations by the Miedema model are estimates, and if possible, the CALPHAD approach should be preferred.

Conclusion

Thus, as a result of a comparison of the thermodynamic characteristics of supersaturated solid solutions based on nickel and aluminum in the Ni-Al system, calculated using two approaches, it was found that the Miedema model, taking into account only the ΔH^{chem} value, gives a good approximation in estimating the enthalpy of supersaturated crystalline solid solutions system, but shows a significant deviation in the calculation of the Gibbs energy. When assessing the enthalpy of formation of metastable phases (amorphous, supersaturated solid solutions) according to the Miedema model, only the chemical interaction of atoms should be taken into account (the ΔH^{chem} in formula (7)). When using the semiempirical Miedema model to determine the enthalpy of formation and Gibbs energy of multicomponent compounds for which there are no data in the reference literature, it should be borne in mind that it can give a significant error (especially for the Gibbs energy), and such calculations should be considered as estimates. The results obtained can be used to assess the thermodynamic parameters of metastable phases formed during MA/Ma and to analyze the effect of preliminary mechanical activation of metal powder systems on subsequent processes of synthesis of new materials, in particular, SHS, reaction sintering, etc.

References

[1] P.R. Soni (2001). Mechanical Alloying: Fundamentals and Applications. [Mekhanicheskoe legirovanie: osnovy i primenenie] Cambridge, UK, Cambridge International Science Publishing.

[2] Sherif M.El-Eskandarany (2015). Mechanical Alloying for Fabrication of Advanced Engineering Materials. [Mekhanicheskoe legirovanie dlya izgotovleniya novejshih inzhenernyh materialov] (Second edition by Sherif M.El-Eskandarany). Amsterdam, Elsevier.

[3] C. Suryanarayana. (2004). Mechanical Alloying and Milling. [Mekhanicheskoe legirovanie i frezerovanie] New York, NY, Marcel Dekker, Inc.

[4] Sereda B.P., Goransky G.G., Khina B.B. (2018). Analysis of thermodynamic characteristics of a multicomponent amorphous iron-based alloy: experimental research and theoretical interpretation. [Analiz termodinamicheskih harakteristik mnogokomponentnogo amorfnogo splava na osnove zheleza: eksperimental'noe issledovanie i teoreticheskaya interpretaciya.] *Science journal Mathematical modeling.* (2(39), 23–28).

[5] Sereda B., Khina B. Kruglyak I. (2020). Thermodynamic analysis of the gas environment in the formation of diffusion coatings using composite saturating charges. [Termodinamicheskij analiz gazovoj sredy pri formirovanii diffuzionnyh pokrytij s ispol'zovaniem kompozitnyh nasyshchayushchih zaryadov] *Metallurgy: Coll. Science. work.* (2 (43)), 43–49.

[6] Sereda B., Hina B., Kruglyak I., Sereda D. (2020). Mathematical modeling of diffusion layers formation using compositional saturating batches charges. [Matematicheskoe modelirovanie formirovaniya diffuzionnyh sloev s ispol'zovaniem kompozicionnyh shiht nasyshchayushchih shiht] *Mathematical modeling.* (2 (43)), 79–85.

[7] A.S.Rogachev, A.S.Mukasyan. (2015). Combustion for Material Synthesis. [Szhiganie dlya sinteza materialov] Boca Raton, FL, CRC Press.

[8] B.B.Khina. (2010). Combustion Synthesis of Advanced Materials. [Sintez peredovyh materialov s pomoshch'yu szhiganiya] New York, Nova Science Publishers.

[9] M.A.Korchagin, T.F.Grigor'eva, B.B.Bokhonov, M.R.Sharafutdinov, A.P.Barinova, N.Z. Lyakhov. (2003). Solid-state combustion in mechanically activated SHS systems. I. Effect of activa-

tion time on process parameters and combustion product composition. [Tverdotel'noe gorenie v mekhanicheski aktiviruemyh sistemah SVS. I. Vliyanie vremeni aktivacii na parametry processa i sostav produktov sgoraniya] *Combustion, Explosion, and Shock Waves*. (1(39)), 43–50.

[10] M.A.Korchagin, T.F.Grigor'eva, B.B.Bokhonov, M.R.Sharafutdinov, A.P.Barinova, N.Z. Lyakhov. (2003). Solid-state combustion in mechanically activated SHS systems. II. Effect of mechanical activation conditions on process parameters and combustion product composition. [Tverdotel'noe gorenie v mekhanicheski aktiviruemyh sistemah SVS. II. Vliyanie uslovij mekhanoaktivacii na parametry processa i sostav produktov sgoraniya] *Combustion, Explosion, and Shock Waves*, (1(39)), 51–58.

[11] A.S.Mukasyan, B.B.Khina, R.V.Reeves, S.F.Son. (2011). Mechanical activation and gasless explosion: Nanostructural aspects. [Mekhanicheskaya aktivaciya i bezgazovyj vzryv: nanostrukturnye aspekty] *Chemical Engineering Journal*, (2-3(174)), 677–686.

[12] S.Stolen, T.Grande, N.L.Allan. (2004). Chemical Thermodynamics of Materials: Macroscopic and Microscopic Aspects. [Himicheskaya termodinamika materialov: makroskopicheskie i mikroskopicheskie aspekty]. Chichester, UK, John Wiley & Sons

[13] A.T. Dinsdale (1991). SGTE data for pure elements. [Dannye SGTE dlya chistyh elementov]. *Calphad*, (4(5)), 317–425.

[14] F.R. de Boer, R.Boom, W.C.M.Mattens, A.R.Miedema, A.K.Niessen (1988). Cohesion and Structures: Cohesion in Metals: Transition Metal Alloys [Svyaznost' i struktury: kogeziya v metallah: splavy perekhodnyh metallov] Amsterdam, Elsevier.

[15] P.I. Loeff, A.W. Weeber, A.R. Miedema. (1990). Diagrams of formation enthalpies of amorphous alloys in comparison with the crystalline solid solution [Diagrammy ental'pij obrazovaniya amorfnyh splavov v sravnenii s kristallicheskim tverdym rastvorom]. *Journal of the Less-Common Metals*, (140), 299–305.

[16] L.J.Gallego, J.A.Somoza, J.A.Alonso. (1990). Glass formation in ternary transition metal alloys. *Journal of Physics: Condensed Matter*, (2), 6245–6250.

[17] A.R.Miedema, P.F. de Chatel, F.R. de Boer. (1980). Cohesion in alloys - fundamentals of a semi-empirical model [Svyaznost' v splavah - osnovy poluempiricheskoj modeli]. *Physica B*, (100), 1–28.

[18] A.W.Weeber, P.I.Loeff, H.Bakker. (1988). Glass-forming range of transition metal-transition metal alloys prepared by mechanical alloying [Diapazon stekloobrazovaniya splavov perekhodnyh metallov i perekhodnyh metallov, poluchennyh metodom mekhanicheskogo legirovaniya]. *Journal of the Less-Common Metals*, (145), 293–299.

[19] A.Niessen, A.R.Miedema. (1983). The enthalpy effect on forming diluted solid solutions of two 4d and 5d transition metals [Vliyanie ental'pii na obrazovanie razbavlennyh tverdyh rastvorov dvuh 4d i 5d perekhodnyh metallov]. *Berichte der Bunsengesellschaft fur physikalische Chemie*, (9(87)), 717–725.

[20] S.P.Sun, D.Q.Yi, H.Q.Liu, B.Zang, Y.Jiang. (2010). Calculation of glass forming ranges in Al-Ni-RE (Ce, La, Y) ternary alloys and their sub-binaries based on Miedema's model [Raschet diapazonov stekloobrazovaniya v trojnyh splavah Al-Ni-RE (Ce, La, Y) i ih sub-dvojnyh komponentah na osnove modeli Midema]. *Journal of Alloys and Compounds*, (1(506)), 377–387.

[21] A.R.Miedema, F.R. de Boer, R.Boom. (1977). Model predictions for the enthalpy of formation of transition metal alloys [Model'nye prognozy ental'pii obrazovaniya splavov perekhodnyh metallov]. *Calphad*, (1(4)), 341–359.

[22] I.Ansara, N.Dupin, H.L.Lukas, B.Sundman. (1997). Thermodynamic assessment of the Al-Ni system[Termodinamicheskaya ocenka sistemy Al-Ni]. *Journal of Alloys and Compounds*, (247), 20–30.

[23] B.Zhang, W.A.Jesser. (2002). Formation energy of ternary alloy systems calculated by an extended Miedema model [Energiya obrazovaniya trojnyh sistem splavov, rasschitannaya po rasshirennoj modeli Midema]. *Physica B: Condensed Matter*, (1-3(315)), 123–132.