Numerical Approach to Predicting Thermodynamic Properties of Ternary Al–Ni–Pt Alloys

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(Received August 18, 2014; revised version March 9, 2015; in final form April 28, 2015)

Thermodynamic properties of ternary Al–Ni–Pt system, such as ${}^{\rm ex}G_{\rm AlNiPt}$, $\mu_{\rm Al(AlNiPt)}$, $\mu_{\rm Ni(AlNiPt)}$, and $\mu_{\rm Pt(AlNiPt)}$ at 1373 K were predicted on the basis of thermodynamic properties of binary systems included in the investigated ternary system. The idea of predicting ${}^{\rm ex}G_{\rm AlNiPt}$ values was regarded as calculation of values of ${}^{\rm ex}G$ function inside a certain area (a Gibbs triangle) unless all boundary conditions, that is values of ${}^{\rm ex}G$ on all legs of the triangle are known (${}^{\rm ex}G_{\rm AlNi}$, ${}^{\rm ex}G_{\rm AlPt}$, ${}^{\rm ex}G_{\rm NiPt}$). This approach is contrary to finding the function value outside a certain area, if the function value inside this area is known. ${}^{\rm ex}$G and L_{ijk} ternary interaction parameters in the Muggianu extension of the Redlich–Kister formalism are calculated numerically using the Mathematica program. The accepted values of the third component concentration x_x differed from 0.01 to 0.1 mol fraction. Values of L parameters in the Redlich–Kister formula vary for different x_x values, the ${}^0L_{\rm AlNiPt}$ value in particular. Values of thermodynamic functions: ${}^{\rm ex}G_{\rm AlNiPt}$, $\mu_{\rm Al(AlNiPt)}$, $\mu_{\rm Ni(AlNiPt)}$ and $\mu_{\rm Pt(AlNiPt)}$ do not differ significantly for different x_x values. The choice of x_x value does not influence the accuracy of calculations.

DOI: 10.12693/APhysPolA.127.1573
PACS: 02.60.Cb, 05.70.Ce

1. Introduction

Aluminide diffusion coatings are widely used for high temperature oxidation and hot corrosion protection of turbine blades used in engine hot sections [1]. These blades are made of nickel-based superalloys [2, 3]. However, aluminide coatings do not fulfill the requirements of long term oxidation resistance at high temperature. Modification of aluminide coatings by platinum is the most effective way to increase their oxidation resistance [4–12]. Coatings are formed in a diffusion process. The information about this process is essential for predicting and influencing the structure and properties of the coatings. Simulation of the diffusion of aluminum, platinum, and nickel requires thorough thermodynamic descriptions of the Al–Ni–Pt system and estimation values of chemical potentials of diffusive elements, $\mu_{\rm Al(AlNiPt)}$, $\mu_{\rm Ni(AlNiPt)}$, and $\mu_{\rm Pt(AlNiPt)}$. Unfortunately, there is no experimental data of the thermodynamic functions of the Al–Ni–Pt system. Nevertheless, there are numerous methods of modeling thermodynamic properties and calculations of phase diagrams in complex systems on the basis of thermodynamic properties and phase diagrams of binary alloys constituting the complex system. One of them is a semi-empirical approach, referred as Calphad method [2, 3, 13]. It is a combination of experimental observation and theoretical modeling and depends on the quality of available experimental data. The basic mathematical method is a minimization of the Gibbs energy of the system for a given temperature, pressure and overall composition. This approach is common to all currently available software packages for the modeling of thermodynamic properties and phase diagrams of multicomponent systems [13].

In this paper a numerical approach to modeling ternary Al–Ni–Pt system on the basis of thermodynamic properties of binary systems included in the investigated ternary system is applied. The idea of predicting ${}^{\rm ex}G_{ijk}$ values is regarded as calculation values of ${}^{\rm ex}G_{ijk}$ function inside a certain area (a Gibbs triangle) unless all boundary conditions, that is values of ${}^{\rm ex}G$ on all sides of the triangle, are known (${}^{\rm ex}G_{ij}$, ${}^{\rm ex}G_{ik}$, ${}^{\rm ex}G_{jk}$). This approach is contrary to finding a function value outside a certain area, if the function value inside this area is known (this issue is well known in mathematics). In this approach, values of excess Gibbs functions for all concentrations of binary alloys are taken into consideration, not only the selected ones and there is no problem with choosing binary mole fractions and proper weighting, unlike in geometrical models [14]. In this approach, weighting of each mole fraction is the same. This model was successfully applied to many alloys (Bi–Cu–Ni, Cu–Sn–Zn, Ag–Au–Bi, In–Sn–Zn, Cu–Fe–Sn, Al–Ni–Pd, Al–Ni–Hf) [13, 15–17] and the results are similar to the values obtained by the Calphad method.

2. Calculations

The excess Gibbs energy ${}^{\rm ex}G_{ijk}$ describes the influence of non-ideal mixing behavior on the thermodynamic properties of a solution phase. The Muggianu [18] extension of the Redlich–Kister formalism [19] is a widely accepted description of the excess Gibbs energy

$$ {}^{\rm ex}G^{\varphi} = \sum_{i\neq j}^{n} x_i x_j \sum_{z=0}^{m} {}^{z}L_{ij}^{\varphi}(x_i - x_j)^z + \sum_{i\neq j\neq k}^{n} x_i x_j x_k L_{ijk}^{\varphi}, \quad (1) $$

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where ${}^{z}L^{\varphi}_{ij}$ are binary and L^{φ}_{ijk} ternary temperature dependent interaction parameters optimized on the basis of the available thermodynamic and phase diagram data.

$$L^{\varphi}_{ijk} = x_i{}^{0}L^{\varphi}x_{ijk} + x_j{}^{1}L^{\varphi}_{ijk} + x_k{}^{2}L^{\varphi}_{ijk}. \quad (2)$$

Binary systems are usually well investigated, therefore values of ${}^{z}L^{\varphi}_{ij}$ parameters are known, but not many ternary alloys have been investigated, so values of L^{φ}_{ijk} parameters for many systems are unknown. Unless the formula (1) and ${}^{z}L^{\varphi}_{ij}$ parameters are known, the idea of calculating L^{φ}_{ijk} parameters can be regarded as the solution of Eq. (2), when all boundary conditions (binary ij alloys) are known. The approach proposed in this paper is as follows: if all boundary conditions, that is ${}^{\mathrm{ex}}G$ values on all sides of the Gibbs triangle (${}^{\mathrm{ex}}G_{ij}$, ${}^{\mathrm{ex}}G_{ik}$, ${}^{\mathrm{ex}}G_{jk}$) (Fig. 1) are known, a value inside the triangle (${}^{\mathrm{ex}}G_{ijk}$) can be found.

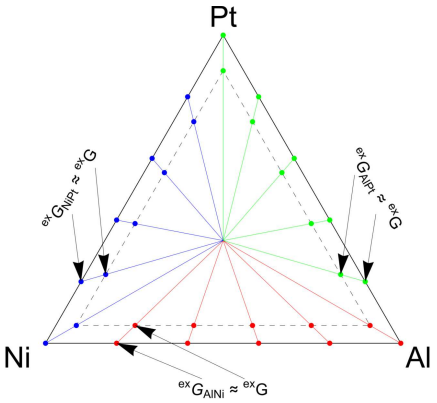

Fig. 1. The Gibbs triangle.

Calculations were performed using the Mathematica program. First, ${}^{\mathrm{ex}}G$ values on all legs of the triangle were calculated and the concentration of the third component was 0. Next, an assumption was made that ${}^{\mathrm{ex}}G$ value on the leg of the triangle and for the small concentration of the third component x_x was the same. L_{ijk} were calculated on the basis of this assumption. The concentration of the third component x_x varied from 0.01 to 0.1 mol fraction. In other words, ${}^{\mathrm{ex}}G$ value for each point of the Gibbs triangle (the bold line) and for the corresponding point of the inner triangle (the dotted line) (see Fig. 1) was assumed to be the same. The concentration of the third component x_x represents the distance between the bold and the dotted lines.

$${}^{\mathrm{ex}}G_{ij} = {}^{\mathrm{ex}}G_{ijk} \text{ for } x_i = 0.01, \quad (3)$$

$${}^{\mathrm{ex}}G_{ik} = {}^{\mathrm{ex}}G_{ijk} \text{ for } x_{\mathrm{j}} = 0.01, \quad (4)$$

$${}^{\mathrm{ex}}G_{jk} = {}^{\mathrm{ex}}G_{ijk} \text{ for } x_{\mathrm{k}} = 0.01. \quad (5)$$

L_{ijk} parameters were calculated numerically on the basis of this assumption using the Mathematica program. In the case of presented calculations, case i, j and k denote Al, Ni and Pt, respectively.

Thermodynamic parameters for binary alloys ${}^{z}L^{\varphi}_{ij}$, ${}^{z}L^{\varphi}_{ik}$, ${}^{z}L^{\varphi}_{jk}$ (formula (1)) were accepted from Huang and Chang [20] for Al–Ni, Wu and Jin [1] for Al–Pt and Lu et al. [12] for Ni–Pt systems.

$$L_{\mathrm{Al,Ni}} = 168292 + 16T + 32712(x_{\mathrm{Al}} - x_{\mathrm{Ni}}) + (7998 + 35T)(x_{\mathrm{Al}} - x_{\mathrm{Ni}})^2, \quad (6)$$

$$L_{\mathrm{Al,Pt}} = -264447 + (102729 - 8.57T)(x_{\mathrm{Al}} - x_{\mathrm{Zr}}), \quad (7)$$

$$L_{\mathrm{Ni,Pt}} = -5000. \quad (8)$$

As a result of calculations the following value of ternary L_{ijk} parameter for 1373 K was obtained on the basis of Eq. (2):

$$L_{\mathrm{Al,Ni,Pt}} = -1.2 \times 10^{-}5x_{\mathrm{Al}} + 9.9 \times 10^{5}x_{\mathrm{Ni}} + 7.7 \times 10^{5}x_{\mathrm{Pt}}. \quad (9)$$

In order to check how much the choice of the x_x value influences the values of L parameters and excess Gibbs energy calculated on the basis on these parameters, analogous calculations were performed for the x_x values 0.01, 0.05, and 0.09. Results of calculations are presented in Table (at the end) and Figs. 2–7. Although values of L parameters change with the x_x value, especially the ${}^{0}L_{\mathrm{AlNiPt}}$ value, the final results, that is the excess Gibbs energy does not change significantly.

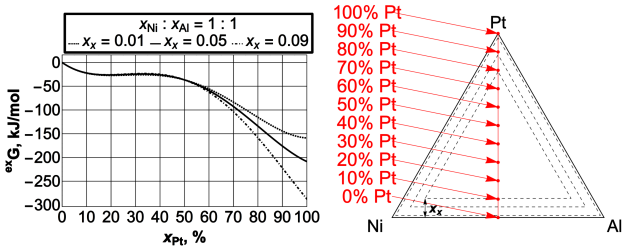

Fig. 2. ${}^{\mathrm{ex}}G_{\mathrm{AlNiPt}}$ for x_{Ni}:x_{Al} = 1:1 for different x_{Pt} values (left) and cross-section (right).

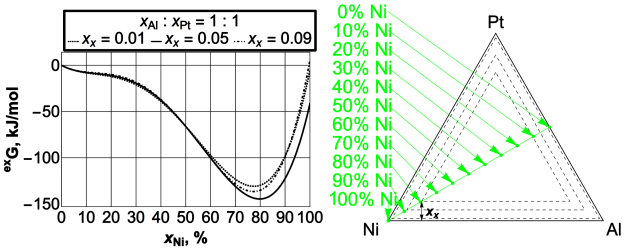

Fig. 3. ${}^{\mathrm{ex}}G_{\mathrm{AlNiPt}}$ for x_{Al}:x_{Pt} = 1:1 for different x_{Ni} values (left) and cross-section (right).

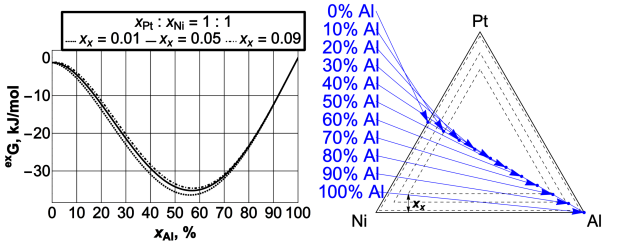

Fig. 4. ${}^{\mathrm{ex}}G_{\mathrm{AlNiPt}}$ for x_{Pt}:x_{Ni} = 1:1 for different x_{Al} values (left) and cross-section (right).

Values of chemical potentials of platinum, nickel and aluminium at 1373 K were derived from the excess Gibbs energy according to the formulae (10)–(12) [21]. Results of calculations are presented in Figs. 5–7.

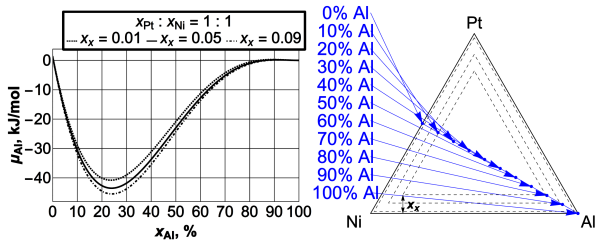

Fig. 5. Values of aluminum chemical potential in Al–Ni–Pt alloys (left) and cross-section (right).

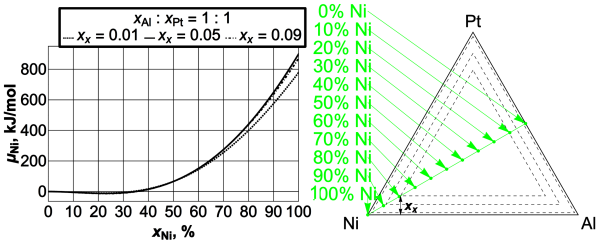

Fig. 6. Values of nickel chemical potential in Al–Ni–Pt alloys (left) and cross-section (right).

$$\mu_{\mathrm{Al}} =^{\mathrm{ex}} G - x_{\mathrm{Ni}}\frac{\partial^{\mathrm{ex}}G}{\partial x_{\mathrm{Ni}}} - x_{\mathrm{Pt}}\frac{\partial^{\mathrm{ex}}G}{\partial x_{\mathrm{Pt}}} =$$
$$5000x_{\mathrm{Ni}}x_{\mathrm{Pt}} + x_{\mathrm{Al}}^2 x_{\mathrm{Ni}}\left(80114x_{\mathrm{Ni}} + 116703.337375x_{\mathrm{Pt}}\right)$$
$$+x_{\mathrm{Al}}\left(-80114x_{\mathrm{Ni}}^3 + x_{\mathrm{Ni}}^2\left(32712 - 1977166.509368x_{\mathrm{Pt}}\right)\right.$$
$$\left.+90962.34x_{\mathrm{Pt}}^2 - 1543546.046419x_{\mathrm{Ni}}x_{\mathrm{Pt}}^2\right), \qquad (10)$$
$$\mu_{\mathrm{Ni}} =^{\mathrm{ex}} G - x_{\mathrm{Al}}\frac{\partial^{\mathrm{ex}}G}{\partial x_{\mathrm{Al}}} - x_{\mathrm{Pt}}\frac{\partial^{\mathrm{ex}}G}{\partial x_{\mathrm{Pt}}} = x_{\mathrm{Al}}\left(-80114x_{\mathrm{Al}}^2 x_{\mathrm{Ni}}\right.$$
$$+x_{\mathrm{Pt}}\left(264446.89 - 988583.254684x_{\mathrm{Ni}}^2 + \right.$$
$$\left.+181924.68x_{\mathrm{Pt}} - 1543546.046419x_{\mathrm{Ni}}x_{\mathrm{Pt}}\right)$$
$$+x_{\mathrm{Al}}\left(80114x_{\mathrm{Ni}}^2 - 181924.68x_{\mathrm{Pt}}\right.$$
$$\left.\left.+x_{\mathrm{Ni}}\left(-32712 + 233406.674749x_{\mathrm{Pt}}\right)\right)\right), \qquad (11)$$
$$\mu_{\mathrm{Pt}} =^{\mathrm{ex}} G - x_{\mathrm{Al}}\frac{\partial^{\mathrm{ex}}G}{\partial x_{\mathrm{Al}}} - x_{\mathrm{Ni}}\frac{\partial^{\mathrm{ex}}G}{\partial x_{\mathrm{Ni}}} = -120171\left(x_{\mathrm{Al}}^3 x_{\mathrm{Ni}}\right.$$
$$+x_{\mathrm{Al}}^2\left(-2x_{\mathrm{Ni}}^2 + x_{\mathrm{Ni}}\left(0.544424 - 1.942288x_{\mathrm{Pt}}\right)\right.$$
$$\left.+0.756941x_{\mathrm{Pt}}\right) + x_{\mathrm{Al}}x_{\mathrm{Ni}}\left(-1.217632 + x_{\mathrm{Ni}}^2\right. \qquad (12)$$
$$\left.\left.+6.422290x_{\mathrm{Pt}}^2 + x_{\mathrm{Ni}}\left(-0.544424 + 16.452942x_{\mathrm{Pt}}\right)\right)\right).$$

3. Conclusions

Values of excess Gibbs energy and chemical potentials of aluminum, nickel, and platinum in ternary Al–Ni–Pt alloys at 1373 K were predicted numerically for three cross-sections (x_{Al}:x_{Ni} = 1:1, x_{Pt}:x_{Ni} = 1:1, x_{Pt}:x_{Al} = 1:1 and for alloys of the following contents: ($x_{\mathrm{Al}} = 1/3$, $x_{\mathrm{Ni}} = 1/3$, $x_{\mathrm{Pt}} = 1/3$, $x_{\mathrm{Al}} = 2/5$, $x_{\mathrm{Ni}} = 2/5$, $x_{\mathrm{Pt}} = 1/5$, and $x_{\mathrm{Al}} = 1/10$, $x_{\mathrm{Ni}} = 4/5$, $x_{\mathrm{Pt}} = 1/10$). The obtained values of the excess Gibbs energy do not change significantly with the change of the predicting procedure, namely the accepted x_x value. The results obtained in this work, that is values of chemical potentials will be used to model the diffusion process in the platinum modified aluminide coatings.

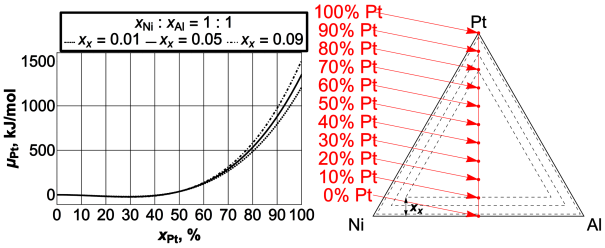

Fig. 7. Values of platinum chemical potential in Al–Ni–Pt alloys (left) and cross-section (right).

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TABLE

The calculated values of L parameters and the excess Gibbs energy.

x_x	${}^0L_{\mathrm{AlNiPt}}$	${}^1L_{\mathrm{AlNiPt}}$	${}^2L_{\mathrm{AlNiPt}}$	${}^{\mathrm{ex}}G_{\mathrm{AlNiPt}}$ $x_{\mathrm{Al}} = x_{\mathrm{Ni}} = x_{\mathrm{Pt}} = 1/3$	${}^{\mathrm{ex}}G_{\mathrm{AlNiPt}}$ $x_{\mathrm{Al}} = x_{\mathrm{Ni}} = 2/5$, $x_{\mathrm{Pt}} = 1/5$	${}^{\mathrm{ex}}G_{\mathrm{AlNiPt}}$ $x_{\mathrm{Al}} = x_{\mathrm{Pt}} = 1/10$, $x_{\mathrm{Ni}} = 4/5$
0.01	-1.2×10^5	9.9×10^5	7.7×10^5	-2.6×10^4	-2.7×10^4	-8.2×10^3
0.02	-1.0×10^5	1.0×10^6	7.9×10^5	-2.5×10^4	-2.7×10^4	-8.1×10^3
0.03	-9.3×10^4	1.0×10^6	8.0×10^5	-2.5×10^4	-2.7×10^4	-8.0×10^3
0.04	-8.3×10^4	1.0×10^6	8.1×10^5	-2.5×10^4	-2.6×10^4	-7.9×10^3
0.05	-7.4×10^4	1.0×10^6	8.1×10^5	-2.4×10^4	-2.6×10^4	-7.8×10^3
0.06	-6.6×10^4	1.1×10^6	8.2×10^5	-2.4×10^4	-2.6×10^4	-7.7×10^3
0.07	-6.1×10^4	1.1×10^6	8.2×10^5	-2.4×10^4	-2.5×10^4	-7.6×10^3
0.08	-5.8×10^4	1.1×10^6	8.2×10^5	-2.3×10^4	-2.5×10^4	-7.5×10^3
0.09	-5.8×10^4	1.1×10^6	8.2×10^5	-2.3×10^4	-2.5×10^4	-7.3×10^3
0.1	-6.2×10^4	1.1×10^6	8.1×10^5	-2.3×10^4	-2.5×10^4	-7.2×10^3