

Calculation of thermodynamic properties in liquid phase for ternary Al–Ni–Zn alloys

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Abstract: The results of the calculation of thermodynamic properties in liquid state for ternary Al–Ni–Zn alloys using the newest version of the general solution model for thermodynamic prediction are presented. Nine sections with different molar ratios of Ni to Zn, Zn to Al and Al to Ni were investigated in a temperature interval of 1800–2000 K. Partial and integral molar thermodynamic properties in liquid phase for the Al–Ni–Zn ternary system are determined and discussed.

Key words: ternary system; Al–Ni–Zn alloys; thermodynamics; calculation; general solution model

1 Introduction

ZA alloys present a group of alloys whose main constituents are zinc and aluminum [1,2]. Originally, they were alloyed with copper and magnesium and developed for gravity casting [3]. But, nowadays, ZA alloys alloyed with other metals, such as Ni, Ga, Ge, Sb, Fe, have a wide variety of demanding applications as engineering materials in different branches of technology: lead-free solders for die attach [4–7], shape memory alloys [8], dental alloys [9,10], coatings for steel sheets [11–13], or as commercial Al bronzes [14,15].

Among numerous ZA alloys, ternary Al–Ni–Zn system due to its structural, mechanical and corrosion resistance properties is used for hot-dip zinc protective coatings on steel exposed to corrosive environments [16,17]. In spite of technological interest for Al–Ni–Zn alloys, this system has not been investigated completely from thermodynamic point of view till now. Insufficient experimental information, mostly due to existing difference between melting temperatures of Ni vs Al and Zn and a high vapour pressure of zinc, caused that mentioned system is still not thermodynamically described [7] although constitutive binary systems Al–Ni

[18], Al–Zn [19] and Ni–Zn [20] are assessed and given in COST531 database [21].

On the other hand, there are more data on Al–Ni–Zn phase equilibria investigations [1,7,16,22–27], but still there is no complete definition. Some literature data on isothermal sections of investigated system at different temperatures are given in Fig. 1.

Having in mind given literature review, available thermodynamic data and difficulties in experimental research of the Al–Ni–Zn system, the purpose of this work was to contribute to better knowledge of its thermodynamic properties in liquid state at high investigating temperatures, using thermodynamic prediction according to the newest version of general solution model.

2 Theoretical fundamentals

The general solution model for calculation of thermodynamic properties for ternary systems based on known binary thermodynamic data has been provided by CHOU and WEI [28,29]. It breaks down the boundary between symmetrical and asymmetrical models, and has already been proved in practical examples as the correct and accurate model [30,31].

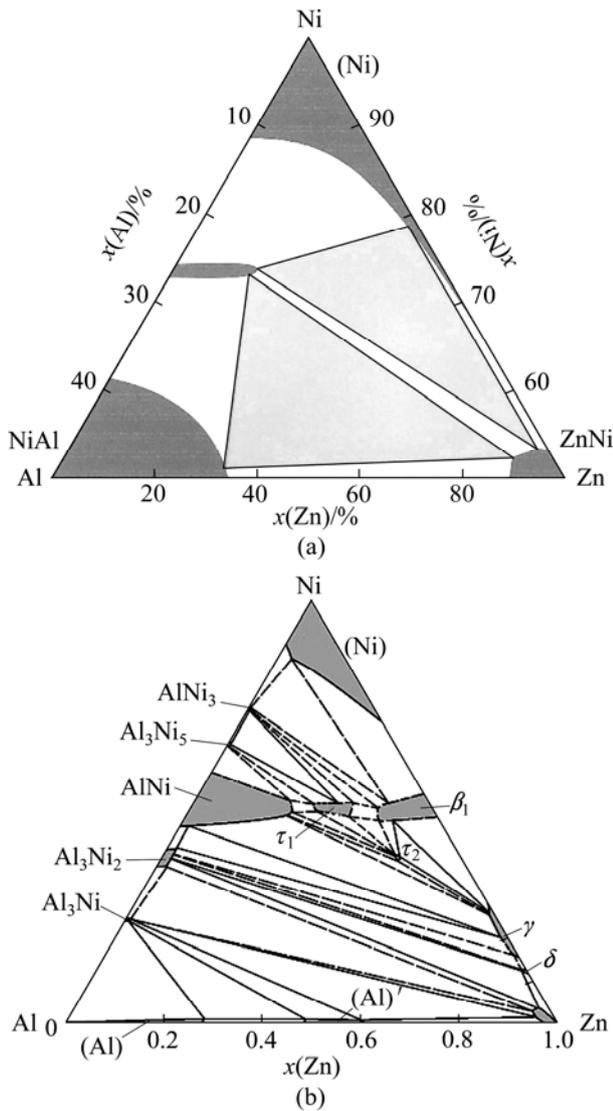


Fig. 1 Isothermal sections of Al–Ni–Zn system at 1123 K [26] (a) and 613 K [16] (b)

This model has been derived for multicomponent systems and its basic equations are given as follows [28]:

$$\Delta G^E = \sum_{i \neq j}^m x_i x_j \left[A_{ij}^0 + A_{ij}^1 \cdot ((x_i - x_j) + \sum_{k=1, k \neq i, j}^m A_{ij}^1 x_k (2\xi_{i(ij)}^{(k)} - 1)) \right] \quad (1)$$

where A_{ij}^0 , A_{ij}^1 , A_{ij}^2 are regular-solution parameters for binary system ij independent of composition, only relying on temperature:

$$\Delta G_{ij}^E = X_i X_j (A_{ij}^0 + A_{ij}^1 (X_i - X_j) + A_{ij}^2 (X_i - X_j)^2 + \dots + A_{ij}^n (X_i - X_j)^n) \quad (2)$$

where X_i and X_j indicate the mole fraction of component i

and j in ij binary system, expressed as

$$X_{i(ij)} = x_i + \sum_{k=1, k \neq i, j}^m x_k \xi_{i(ij)}^{(k)} \quad (3)$$

and where the coefficient signed as $\xi_{i(ij)}^{(k)}$ in Eq. (1) presents the similarity coefficient of component k to component i in ij system, defined as

$$\xi_{i(ij)}^{(k)} = \frac{\eta(ij, ik)}{\eta(ij, ik) + \eta(ji, jk)} \quad (4)$$

where $\eta(ij, ik)$ is the function related to the excess Gibbs free energy of ij and ik binaries, given as

$$\eta(ij, ik) = \int_{X_i=0}^{X_i=1} (\Delta G_{ij}^E - \Delta G_{ik}^E)^2 dX_i \quad (5)$$

Recently, the newest version of general solution model based on Redlich–Kister type parameters was presented in Ref. [32]. The calculations using this innovated model substituted a series of integration processes in older model version with simplified calculation. Since a large number of real systems can be approximately fitted by a Redlich–Kister polynomial [33], a new formalism presents an advantage. The whole integration process is avoided by using algebraic operations, thereby simplifying the calculation.

Main changes in comparison with old model [28] are related to determination of $\eta(ij, ik)$ function, as follows [32]:

$$\begin{aligned} \eta_I &= \sum_{i=0}^n \frac{1}{2(2i+1)(2i+3)(2i+5)} (A_{12}^i - A_{13}^i)^2 + \\ &\sum_{j=0, k>j}^n \frac{1}{(j+k-1)(j+k+3)(j+k+5)} \cdot \\ &(A_{12}^j - A_{13}^j)(A_{12}^k - A_{13}^k) \\ \eta_{II} &= \sum_{i=0}^n \frac{1}{2(2i+1)(2i+3)(2i+5)} (A_{21}^i - A_{23}^i)^2 + \\ &\sum_{j=0, k>j}^n \frac{1}{(j+k-1)(j+k+3)(j+k+5)} \cdot \\ &(A_{21}^j - A_{23}^j)(A_{21}^k - A_{23}^k) \\ \eta_{III} &= \sum_{i=0}^n \frac{1}{2(2i+1)(2i+3)(2i+5)} (A_{31}^i - A_{32}^i)^2 + \\ &\sum_{j=0, k>j}^n \frac{1}{(j+k-1)(j+k+3)(j+k+5)} \cdot \\ &(A_{31}^j - A_{32}^j)(A_{31}^k - A_{32}^k) \end{aligned} \quad (6)$$

where A_{ij}^k are the Redlich–Kister polynomials. It should be pointed out that $A_{ij}^k = (-1)^k A_{ji}^k$. Based on Eq. (6), main Eq. (1) presenting can be written as follows [32]:

$$\begin{aligned} \Delta G^E = & x_1 x_2 \sum_{i=0}^n A_{12}^i [x_1 - x_2 + (2\xi_{12} - 1)x_3]^i + \\ & x_2 x_3 \sum_{i=0}^n A_{23}^i [x_2 - x_3 + (2\xi_{23} - 1)x_1]^i + \\ & x_3 x_1 \sum_{i=0}^n A_{31}^i [x_3 - x_1 + (2\xi_{31} - 1)x_2]^i \end{aligned} \quad (7)$$

In all equations given, ΔG^E and ΔG_{ij}^E respond to the integral molar excess free energies for multicomponent and binary systems, respectively, while x_1 , x_2 , x_3 respond to mole fraction of components in investigated multicomponent system.

3 Results and discussion

Thermodynamic calculations in ternary system Al–Ni–Zn were carried out in nine sections along the lines of constant molar ratio of Ni to Zn of 1:3, 1:1, 3:1, sections from aluminium corner; molar ratio of Zn to Al of 1:3, 1:1, 3:1, sections from nickel corner; and molar ratio of Al to Ni of 1:3, 1:1, 3:1, sections from zinc corner. Basic data necessary for the calculation have been taken from Refs. [18–21]. The Redlich–Kister polynomials for the constitutional binaries in the investigated ternary Zn–Ni–Al system are presented in Table 1.

The prediction is done according to the fundamentals of the newest version of general solution model [32]. Based on starting data in Table 1, similarity

coefficients are determined and further calculations are carried out for 81 alloys in all selected cross sections in the investigated ternary Al–Ni–Zn system in temperature interval of 1800–2000 K, as given by Eqs. (1–7).

The results of thermodynamic predictions, including the values of ternary integral molar excess Gibbs energy and the activities of all three components in liquid phase, are calculated for all investigated sections at all investigated temperatures, and presented in Table 2, Figs. 2 and 3, respectively. Calculated activity values for all three components are used for construction of isoactivity diagrams at 1900 K and shown in Fig. 4.

Negative values of integral molar excess Gibbs energies are obtained for whole concentration range at all investigated temperatures (Fig. 2). The most negative value of about –35 kJ/mol is present in the section from zinc corner with molar ratio of Al to Ni of 1:1 for low zinc concentration, while other minimal values of about –25 kJ/mol are noticed for equiatomic contents in the $n(\text{Ni}):n(\text{Zn})=3:1$ section from aluminum corner and in the $n(\text{Zn}):n(\text{Al})=3:1$ section from nickel corner.

Negative deviation from Raoult law is obtained for all investigated sections (Fig. 3), except in narrow composition ranges: for sections from zinc corner, $x(\text{Zn}) < 0.7$ in $n(\text{Al}):n(\text{Ni})=1:1$ and $x(\text{Zn}) < 0.9$ in $n(\text{Al}):n(\text{Ni})=3:1$; for all three sections from nickel corner, $x(\text{Ni}) > 0.9$, where a very slight positive deviation can be seen. The strongest negative deviation is noticed for section $n(\text{Ni}):n(\text{Zn})=3:1$ from aluminum corner.

Table 1 Redlich–Kister parameters for liquid phase in constitutional binaries in Al–Ni–Zn system

System ij	$A_{ij}^0(T)$	$A_{ij}^1(T)$	$A_{ij}^2(T)$	$A_{ij}^3(T)$	$A_{ij}^4(T)$
Al–Ni [18]	$-207109.28+41.31501T$	$-10185.79+5.8714T$	$81204.81-31.95713T$	$4365.35-2.51632T$	$-22101.64+13.16341T$
Ni–Zn [19]	$-50721.64+7.34178T$	$8436.3+1.97211T$	$-25136.08+11.79072T$	–	–
Al–Zn [20]	$10465.55-3.39259T$	–	–	–	–

Table 2 Characteristic dependencies of ternary integral molar excess energies on composition for ternary Al–Ni–Zn alloys expressed as $\Delta G^E = Ax^2 + Bx + C$ at investigated temperatures

Section	1800 K			1900 K			2000 K		
	A	B	C	A	B	C	A	B	C
$n(\text{Al}):n(\text{Ni})=1:3$	2239.94	19910.37	–23577.77	2208.13	19307.92	–22937.91	2176.43	18705.44	–22298.08
$n(\text{Al}):n(\text{Ni})=1:1$	–18228.38	50071.26	–32961.63	–17331.31	48153.19	–31908.49	–16433.86	46234.91	–30855.41
$n(\text{Al}):n(\text{Ni})=3:1$	–17747.08	40896.18	–23630.54	–16984.37	39450.61	–22932.65	–16221.24	38004.76	–22234.83
$n(\text{Ni}):n(\text{Zn})=1:3$	19142.62	–10429.99	–8343.98	18635.04	–10130.50	–8168.71	18127.89	–9831.45	–7993.41
$n(\text{Ni}):n(\text{Zn})=1:1$	54576.51	–43992.02	–9403.99	52721.09	–42426.83	–9218.89	50866.39	–40862.34	–9033.76
$n(\text{Ni}):n(\text{Zn})=3:1$	94843.85	–87175.70	–5885.86	91812.51	–84444.65	–5713.04	88781.78	–81714.18	–5540.20
$n(\text{Zn}):n(\text{Al})=1:3$	62817.77	–61723.67	461.31	61246.36	–60060.04	402.53	59675.05	–58396.51	343.74
$n(\text{Zn}):n(\text{Al})=1:1$	86518.03	–86079.66	1100.76	83832.84	–83369.68	1002.32	81148.10	–80660.07	903.84
$n(\text{Zn}):n(\text{Al})=3:1$	111033.30	–110659.42	1235.94	107314.19	–107020.10	1138.54	103595.67	–103381.24	1041.10

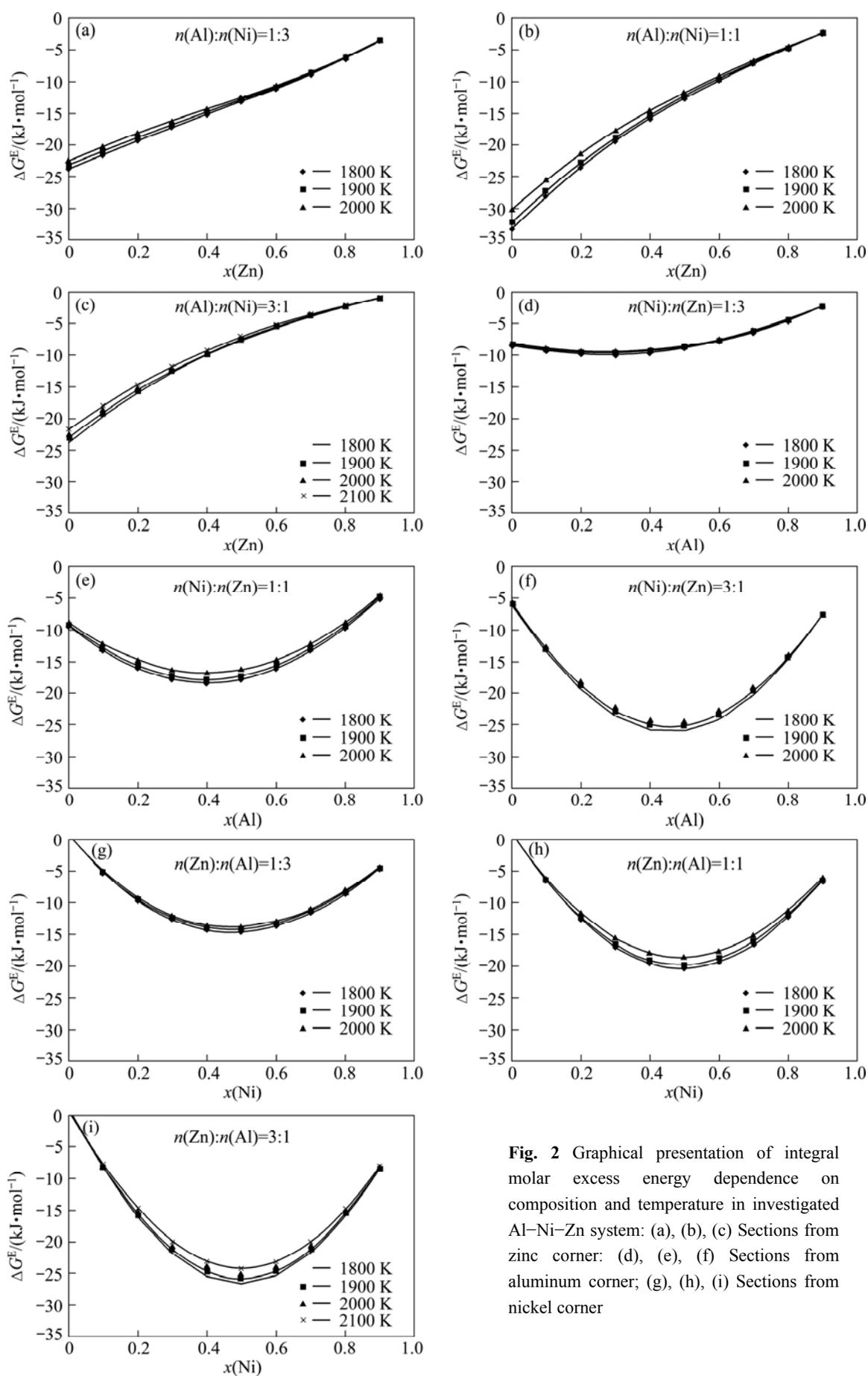


Fig. 2 Graphical presentation of integral molar excess energy dependence on composition and temperature in investigated Al-Ni-Zn system: (a), (b), (c) Sections from zinc corner; (d), (e), (f) Sections from aluminum corner; (g), (h), (i) Sections from nickel corner

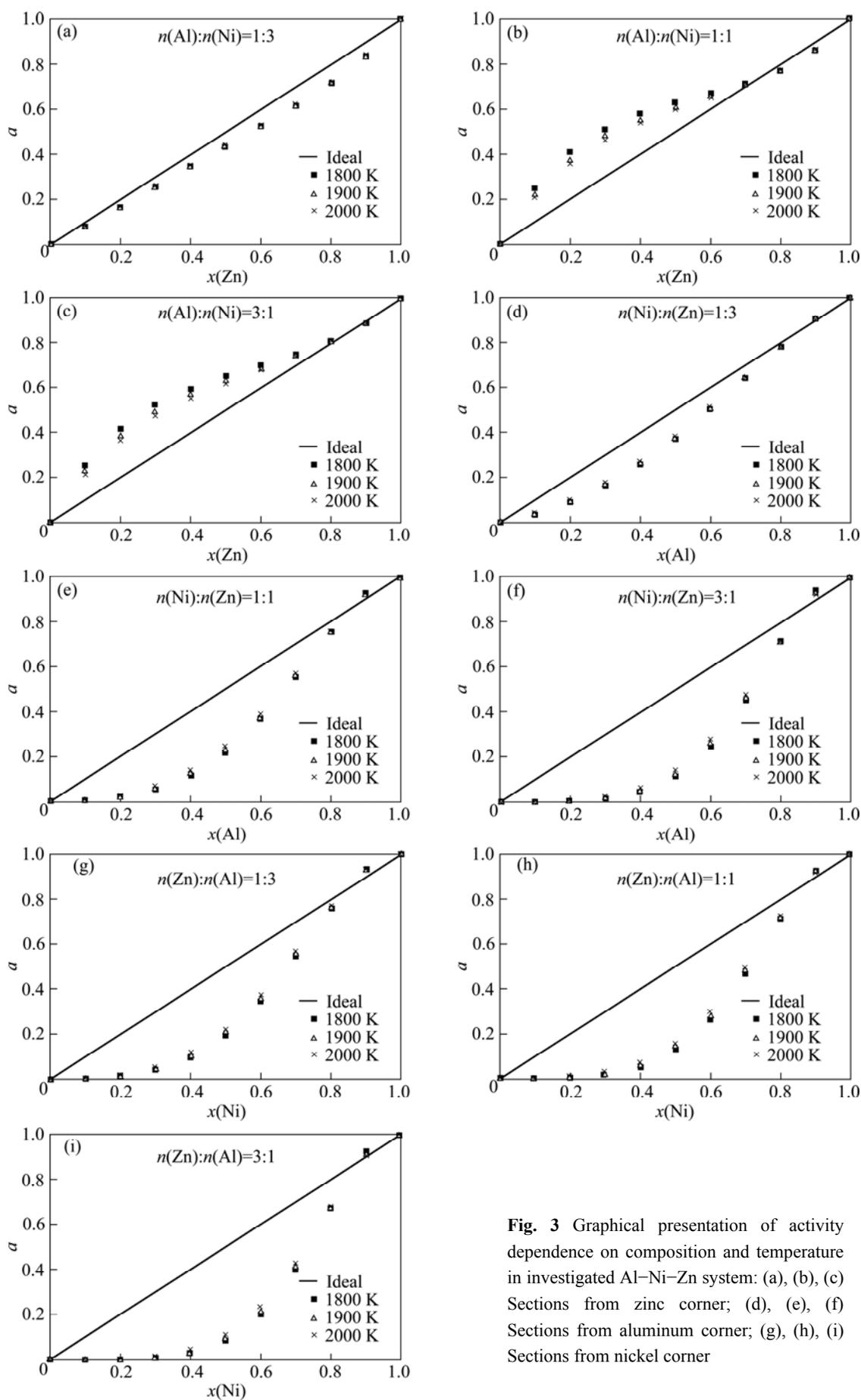


Fig. 3 Graphical presentation of activity dependence on composition and temperature in investigated Al-Ni-Zn system: (a), (b), (c) Sections from zinc corner; (d), (e), (f) Sections from aluminum corner; (g), (h), (i) Sections from nickel corner

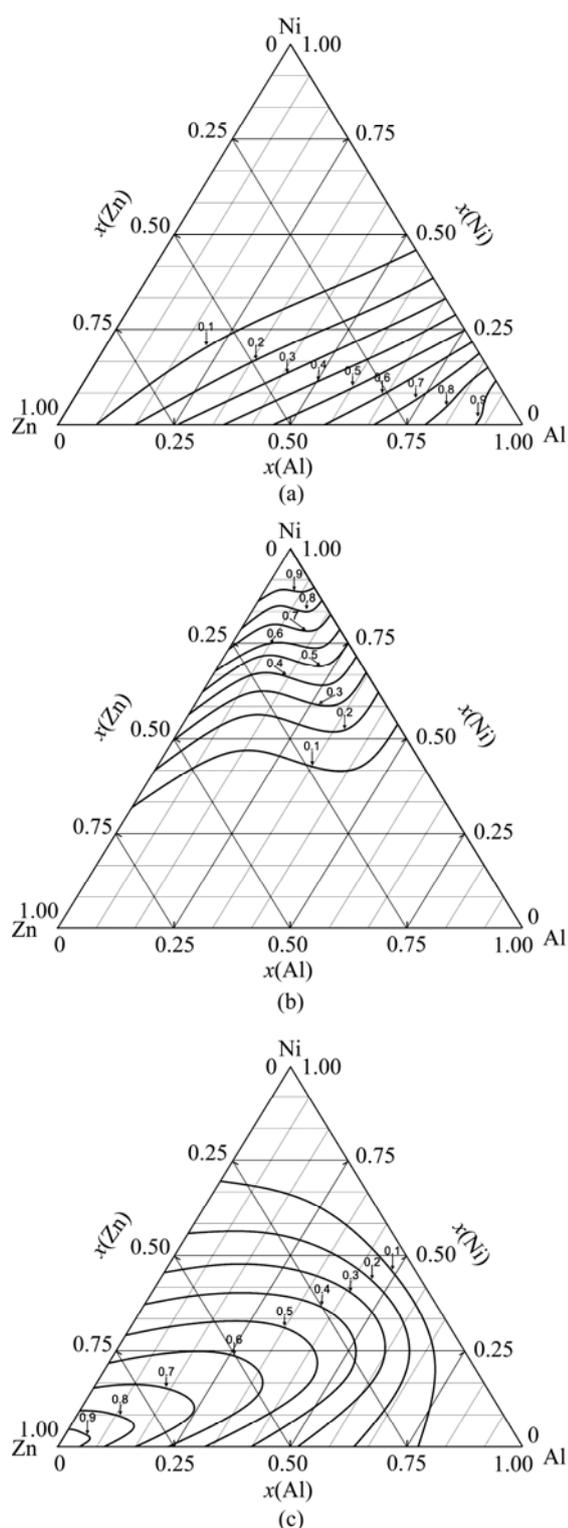


Fig. 4 Isoactivity diagrams for constitutive elements in ternary Al–Ni–Zn system at 1900 K: (a) Aluminum; (b) Nickel; (c) Zinc

Temperature influence on calculated thermodynamic properties is not significant in investigated interval of 1800–2000 K.

Described tendencies indicate to prevalent existence of strong mutual mixing tendencies between constitutive

components in Al–Ni–Zn system at investigated temperatures, where aluminum and nickel exhibit more significant mixing tendency compared with zinc.

4 Conclusions

1) The calculation of thermodynamic properties in ternary Al–Ni–Zn system has been done applying the newest version of general solution model for multicomponent systems based on Redlich–Kister type parameters. According to starting thermodynamic data for constituent binary subsystems, ternary integral molar excess Gibbs energies and activities for all three components were calculated in the temperature range of 1800–2000 K in nine sections from zinc, aluminum and nickel corner. Obtained data showed mostly negative deviation from Raoult law, indicating strong mutual mixing tendencies in the investigation system.

2) Due to the fact that experimental determination at selected temperatures is rather difficult and that there is a lack of relevant literature concerning this particular system, these calculated results can be a good substitution for thermodynamic data of this multicomponent ZA-based system. That is more important, having in mind already proven accuracy of calculation model applications in different cases.

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液相三元 Al–Ni–Zn 合金的热力学性质计算

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摘 要: 将用于热力学预测的最新版本的通用模型用来计算液相三元 Al–Ni–Zn 合金的热力学性质。对 9 个具有不同 Ni 与 Zn, Zn 与 Al 和 Al 与 N 摩尔比的截面在 1800~2000 K 的热力学性质进行研究。对液相三元 Al–Ni–Zn 合金的局部和整体的摩尔热力学性质进行了测定, 并对结果进行了讨论。

关键词: 三元系; Al–Ni–Zn 合金; 热力学; 计算; 通用溶液模型

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