Journal of Applied and Advanced Research 2016, 1(4): 14–17
doi.: 10.21839/jaar.2016.v1i4.37
http://www.phoenixpub.org/journals/index.php/jaar

Research Article – Material Science

Thermodynamic investigation of liquid properties of the Ni–Sn–Ti ternary system using CALPHAD method and geometric models

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Abstract

Predictions for the liquid Ni–Sn–Ti alloys thermodynamic properties (molar excess Gibbs energy) are presented. The calculations were performed in the temperature range 1000–2000 K. Geometric models (using data from the binary end-systems) were used and the respective calculated molar excess Gibbs energy values were compared to CALPHAD method assessments. The concentration dependences of the liquid phase thermodynamic properties along different vertical sections Sn:Ti, Ni:Ti and Ni:Sn were estimated. Ternary interaction parameters (L_0, L_1 and L_2) of the liquid phase were determined using General solution (geometric) model from thermodynamic data of the binary end–systems (Ni–Sn, Ni–Ti, Sn–Ti). Ternary parameters exhibit values: L_0 = - 70360.5 - 0.263*T; L_1 = -113023 - 11.574*T; L_2 = -131755 - 17.101*T. Negative molar excess Gibbs energies were obtained by all models.

Key words: General solution model, Ternary interaction parameters, Ternary systems, CALPHAD method

Introduction

The Ni–Sn–Ti system is important for the interesting as potential lead-free, high temperature solder materials McCormack *et al.* (1994). The first experimental studies of phase equilibria in the Ni–Sn–Ti ternary system were performed by Stadnyk *et al.* (1991). They presented isothermal section at 773 K. Two type of compounds half-Heusler and Heusler were found in the system. Recently the system was investigated from Gürth *et al.* (2015) by isothermal section and phase equilibria and Berche *et al.* (2016) using three binary systems. The binary systems were thermodynamically investigated and used in the calculations. Three systems: Ni–Sn Gandova (2016), Liu *et al.* (2004), Ni–Ti Gandova (2016), Tokunaga *et al.* (2004) and Sn–Ti Yin *et al.* (2007) exibit large number of intermediate phases.

The task of the present study is to verify different ways to achieve thermodynamic assessment of a ternary phase (in this case, the liquid solutions of the system Ni–Sn–Ti) by assessing the thermodynamic properties of the liquid phase using the general solution model (GSM), other geometrical models and comparing to values, obtained by the CALPHAD method.

Theoretical fundamentals

Thermodynamic properties of the Ni–Sn–Ti system was calculated using general solution model Chou (1995), Chou *et al.* (1997) based on three corresponding binary systems.

Chou (1995) was developed a method called general solution model (GSM) for calculation of a ternary phase thermodynamic properties. The application of this model requires some thermo chemical information about the three binary end-systems. Such information was essentially known if the composition and temperature dependence of the Gibbs molar excess energy of a phase was available. In the equations below, the following

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Received: 16-11-2016; Accepted 07-12-2016; Published Online 09-12-2016

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excess energies were represented: ΔG^E – Gibbs molar excess energy of the ternary liquid phase; ΔG^E_{12}, ΔG^E_{23}, ΔG^E_{31} or ΔG^E_{ij} – the respective Gibbs molar excess energy values of the binary liquid phases, where the down indexes indicate the considered binary system.

The composition dependence of the binary Gibbs molar excess energies was given by the expression:

$$\Delta G^E = x_1x_2\Delta G^E_{12} + x_2x_3\ \Delta G^E_{23} + x_3x_1\ \Delta G^E_{31} + x_1x_2x_3\, f_{123} \qquad (1)$$

$$\Delta G^E_{123} = X_1 X_2 X_3 L_{123} \qquad (2)$$

where L_{123} is a ternary interaction parameter that might be temperature and concentration dependent.

Kohler (1960) presented Gibbs molar excess energy of the ternary liquid phase as symmetrical model. Mugiany *et al*. (1975) presented Gibbs molar excess energy of the ternary liquid phase as asymmetrical model. In the general case, a ternary system with constituents 1, 2 and 3 was considered where X_1, X_2 and X_3 were the mole fractions of the respective components 1-Ni, 2-Sn and 3-Ti. Basic thermodynamic information on the binary subsystems was presented in Table 1.

Results and Discussion

Calculations of the coefficients f_{123} were done along three sections of the Ni–Sn–Ti system with different molar ratios in the interval 1000–2000 K. In such a way a huge amount of information was obtained and used thereafter to derive the parameters L_{ijk}. The results are shown in Table 2.

The ternary integral molar Gibbs excess energies assessed by geometrical models were graphically compared to these obtained by Thermo-Calc, using the optimized adjustable parameters of the end-systems only (Table 1). Sections with constant molar ratios between two of the components were plotted.

Figures 1-3 presented calculated in this work molar excesses Gibbs energies at 2000 K and 1:3 molar ration in different mole fractions between Sn:Ti, Ni:Ti and Ni:Sn. Figure 1 presented calculation of Sn:Ti=1:3 mole fractions in the ststem. In Figure 1 curve obtained by GSM model is closed with Mugiany model curve, but curves obtained by TC and model of Kohler are closed too.

Figure 1. Calculated in this work molar Gibbs excess energies (ΔG^E, J mol^{-1}) of the liquid phase, along a section with constant molar Sn:Ti ratio at 2000 K.

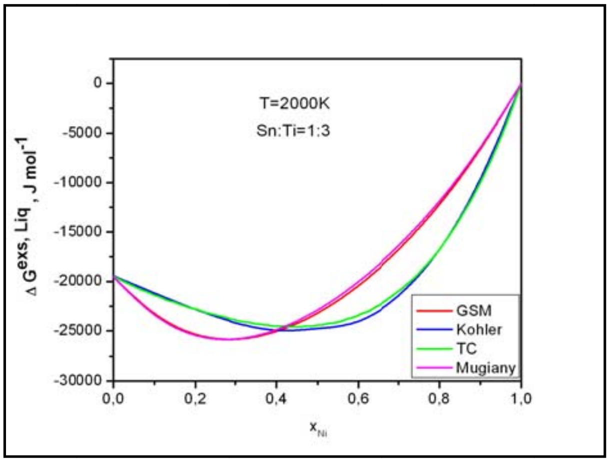


Figure 2. Calculated in this work molar Gibbs excess energies (ΔG^E, J mol^{-1}) of the liquid phase, along a section with constant molar Ni:Ti ratio at 2000 K.

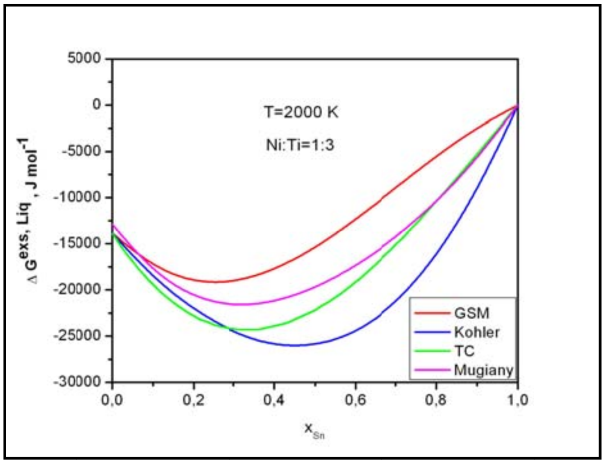


Figure 2 presented calculations at 2000 K and Ni:Ti=1:3 mole fractions. In the Figure seen that calculations obtained by GSM model exhibit the high Gibbs excess energy with minimum at 0.25 mole fractions Sn. The Gibbs energy was the lower calculated by Kohler model. The minimum was at 0.5 mole fractions Sn and -25000 J mol^{-1}. Figure 3 presented investigation system at Ni:Sn=1:3 mole fractions. In this case the smallest Gibbs excess energy seen in calculations preparing

Table 1. Optimized parameters (L^{o}_{ij}, L^{1}_{ij} , L^{2}_{ij}) for the liquid binary phases of the Ni–Sn, Ni–Ti and Sn–Ti systems used in the present work; T – temperature, K.

System, i – j	L^{o}_{ij} (T), J mol^{-1}	L^{1}_{ij} (T), J mol^{-1}	L^{2}_{ij} (T), J mol^{-1}
Ni–Sn	-105002.87+197.9*T -21.6959*T*LN(T)	-28342.17+52.5528*T -7.56094*T*LN(T)	+5582.31
Ni–Ti	-153707.39+34.85*T	-81824.755+25.809*T	-10.077897*T
Sn–Ti	-91598.9-.9416*T	+45682.64-12.1045*T	0

Table 2. Ternary interaction parameters, L^{v}_{ijk}, for the Ni–Sn–Ti liquid phase obtained from the f_{123} coefficients. T – temperature, K.

System, ijk	L^{o}_{ijk} (T), J mol^{-1}	L^{1}_{ijk} (T), J mol^{-1}	L^{2}_{ijk} (T), J mol^{-1}
Ni-Sn-Ti	- 70360.5 - 0.263*T	- 113023 -11.574*T	- 131755 -17.101*T

with model of Kohler around -18000 J mol^{-1} and 0.35 mole fractions Ti. The curves obtained by GSM model and Mugiany model have coincidence. Minimum Gibbs energy observed with TC calculations around -25 000 J mol^{-1} and 0.55 mole fractions Ti. In all figures and sections observed negative Gibbs energys.

Figure 4 presented ternary molar Gibbs excess energies using GSM model at three different temperatures and compared. Results after calculations showed that with increase of temperature the Gibbs excess energy decrease to positive values. At 1943 K the Gibbs excess energy exhibit minimum around -18000 J mol^{-1} but at 2343 K exhibit minimum around -15000 J mol^{-1}. In this case could be conclude that appeared dependence between temperature and Gibbs excess energies

Figure 3. Calculated in this work molar Gibbs excess energies (ΔG^E, J mol^{-1}) of the liquid phase, along a section with constant molar Ni:Sn ratio at 2000 K.

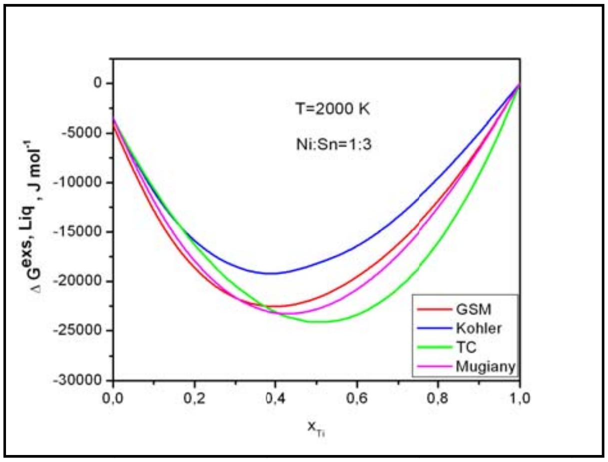
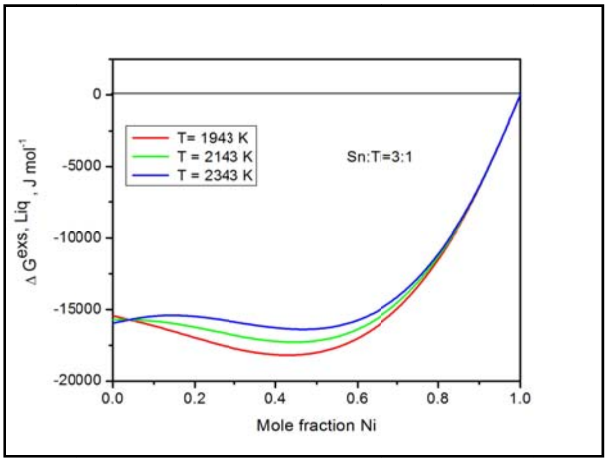


Figure 4. Calculated molar Gibbs excess energies of the liquid phase in three different temperatures according to GSM models.



Conclusions

Thermodynamic properties calculated of liquid phase in the Ni–Sn–Ti ternary system were investigated using general solution model (GSM). The ternary interaction coefficients were obtained at various temperatures and different constant ratios between elements. The values of the ternary liquid phase molar Gibbs excess energies calculated by GSM were compared to values obtained by others models. Negative molar Gibbs energies were seen at all cases. The results may serve and apply when no found experimental data in the investigated system.

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