

# Thermodynamic Description of Ni Based Binary Phase Diagrams

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## Abstract

Ni based binary alloys are commonly used to replace lead in the electronics and other devices. Thermodynamic investigation of two binary systems containing Ni was performed. Calphad method was used for thermodynamic description of same solid phases. In two systems three binary phases are remodeled. The enthalpies of formation of all solid phases were calculated and compared by two methods.

**Keywords:** Binary phase diagrams, Thermodynamic modeling, Calphad method.

## 1. Introduction

The Ni based alloys are used in different industries of the soldering technologies in controlling the mechanical and electric properties. The reason for this interest is that these alloys are prospective for development of lead-free solders [1, 2]. The intermetallic compounds play an important role exhibit different properties connected with content of Ni. Material science knowledge connected with reactions between Ni and solders in interface.

### 1.1 Ni–Sn binary system

The Ni–Sn binary system consists of the liquid, bct\_A5, fcc\_A1, Ni<sub>3</sub>Sn<sub>HT</sub>, Ni<sub>3</sub>Sn<sub>LT</sub>, Ni<sub>3</sub>Sn<sub>2HT</sub>, Ni<sub>3</sub>Sn<sub>2LT</sub> and Ni<sub>3</sub>Sn<sub>4</sub> as stable phases. A detailed investigation of the Ni–Sn system was published by Nash and Nash [3]. Their work was the basis of the Ni–Sn phase diagram published in the compilation by Massalski et al. [4]. The liquidus temperature of the Ni–Sn system together with the solidus it was determined by a number of authors using the thermal analysis [5-7]. The system was investigated of Schmetterer et al. [8] using XRD (including high temperature XRD), DTA, EPMA and metallographic analysis. Leineweber et al. [9-12] first discovered two incommensurate Ni<sub>3</sub>Sn<sub>2</sub> low-temperature modifications. Glibin et al. [13] determined standard enthalpies of formation, entropies and molar heat capacities for a number of phases of Ni–Sn system by graphical and analytical methods.

The mixing enthalpies of liquid Ni–Sn alloys were measured through calorimetry by Haddad et al. [14]. The mixing enthalpies of the solid phases were determined through calorimetry by Flandorfer et al. [15].

The optimization of binary Ni–Sn system was performed by Gosh et al. [16]. He described phase as Ni<sub>3</sub>Sn (high and low temperature) (Ni,Sn)<sub>3</sub>(Sn,Ni), Ni<sub>3</sub>Sn<sub>2</sub> (high-temperature) as (Ni)(Sn)(Ni,Va), Ni<sub>3</sub>Sn<sub>2</sub> (low-temperature) as (Ni)(Sn)(Ni,Va)<sub>0.5</sub>(Ni,Va)<sub>0.5</sub> and Ni<sub>3</sub>Sn<sub>4</sub> as (Ni)<sub>3</sub>(Sn,Ni)<sub>4</sub> using sublattice models. Mietinen [17] reassessed it when assessing the Cu–Ni–Sn phase diagram. His Ni–Sn description was simplified by treating the Ni<sub>3</sub>Sn<sub>2</sub> phase as one phase and modeled with two sublattice model as (Ni)<sub>0.6</sub>(Sn)<sub>0.4</sub>. Another phases Ni<sub>3</sub>Sn (high and low temperature) and Ni<sub>3</sub>Sn<sub>4</sub> described with two sublattice models. In both optimizations phase Ni<sub>3</sub>Sn<sub>4</sub> is treated as stoichiometric compound.

The last optimization of Ni–Sn system was done by Liu et al. [18] and Zemanova et al. [19]. The intermetallic phases in the system were described with sublattice models [18]. They treated phase Ni<sub>3</sub>Sn<sub>2</sub> as two phases high and low temperature as: Ni<sub>3</sub>Sn<sub>2HT</sub> and Ni<sub>3</sub>Sn<sub>2LT</sub>, while [19] treated same phase as one phase Ni<sub>3</sub>Sn<sub>2</sub>.

### 1.2 Ni–Ti phase diagram

The phase diagram of the Ni–Ti system was studied more. Poole et al. [20] were reported data on the liquidus and solidus for the Ni-rich side of the Ni–Ti system using thermal analysis. Their data do not agree with each other. Kajikawa et al. [21] investigated the liquidus and solidus for the Ni-rich side of the Ni–Ti system too. There measurements connected to establish the phase equilibria between the liquid and Fcc phases. Zhou et al. [22] investigated system by diffusion couples technique. It was found that both Ti<sub>2</sub>Ni and TiNi<sub>3</sub> layer form at the Ni–Ti interface in all couples treated by different process.

The enthalpies of formation of liquid Ni–Ti alloys were measured independently with two different calorimeters, one at 1741 and the other at 1838 K by Luck et al. [23]. Gachon et al. [24, 25] measured the enthalpies of formation of the binary compounds in the Ni–Ti system by direct reaction calorimetry at high temperatures.

The binary Ni–Ti system was evaluated by Murray [26]. Three intermetallic compounds were formed: Ni<sub>3</sub>Ti, NiTi and NiTi<sub>2</sub>. Ni<sub>3</sub>Ti and NiTi are melted congruently, while NiTi<sub>2</sub> was formed peritectically. Although Ni<sub>3</sub>Ti had no homogeneity range in its evaluation. Jia et al. [27] reported a homogeneity range for this phase. The Ni–Ti

system was thermodynamically evaluated by Kaufman et al. [28], Saunders [29], Liang et al. [30], Bellen et al. [31], Tokunaga et al. [32] and Keyzer et al. [33]. In the work of Kaufman et al. [28], all intermediate phases are described as the stoichiometric compounds. Saunders [29] applied the two-sublattice model with the formula  $(\text{Ni},\text{Va})_{0.5}(\text{Ni},\text{Ti})_{0.5}$  to describe NiTi phase. The Ni–Ti system was reevaluated by Liang et al. [30]. A subregular solution model was used for the liquid and regular for the terminal solid solutions ( $\alpha$  Ti), ( $\beta$  Ti), (Ni). The compounds,  $\text{Ti}_2\text{Ni}$  and  $\text{TiNi}_3$ , are treated as line compounds (stoichiometric phases), while NiTi was described by a three-sublattice model. Bellen et al. [31] used suitable sublattice models to describe the non-stoichiometries of NiTi and  $\text{Ni}_3\text{Ti}$ . For NiTi phase they

used three sublattice model  $(\text{Ni},\text{Ti})_{0.5}(\text{Ni},\text{Ti})_{0.5}(\text{Va})_3$ , but for phase  $\text{Ni}_3\text{Ti}$  two sublattice model  $(\text{Ni})_{0.75}(\text{Ni},\text{Ti})_{0.25}$ . Tokunaga et al. [32] assessed phase diagram Ni–Ti and extrapolated to ternary Ni–Si–Ti system using experimental information and ab initio calculations. Intermediate phases were modeled with two sublattice models as:  $\text{Ni}_3\text{Ti}$   $(\text{Ni},\text{Ti})_{0.75}(\text{Ni},\text{Ti})_{0.25}$ ,  $\text{NiTi}$   $(\text{Ni},\text{Va})_{0.5}(\text{Ni},\text{Ti})_{0.5}$ ,  $\text{NiTi}_2$   $(\text{Ni})_{0.33}(\text{Ti})_{0.67}$ . Partial reassessment of the binary Ni–Ti system was made by Keyzer et al. [33] with the Calphad method and using the compound energy formalism (CEF). There optimization was extrapolated to ternary Fe–Ni–Ti system. Table 1 shows crystal structures of binary Ni–Sn and Ni–Ti systems.

Table 1. Crystal structures of pure components and binary phases in systems Ni–Sn and Ni–Ti.

Phase name	Pearson symbol	Prototype	Space group	Strukturberich designation	Wyckoff positions	References
(Ni)	<i>cF4</i>	Cu	$Fm\bar{3}m$	A1	a	[4]
( $\beta$ Sn)	<i>tI4</i>	Sn	$I41/amd$	A5	b	[4]
( $\alpha$ Ti)	<i>hP2</i>	Mg	$P6_3/mmc$	A3	c	[4]
( $\beta$ Ti)	<i>cI2</i>	W	$Im\bar{3}m$	A2	a	[4]
$\text{Ni}_3\text{Sn}$ HT	<i>cF16</i>	$\text{BiF}_3$	$Fm\bar{3}m$	$D0_3$	abc	[9]
$\text{Ni}_3\text{Sn}$ LT	<i>hP8</i>	$\text{Ni}_3\text{Sn}$	$P6_3/mmc$	$D0_{19}$	...	[9]
$\text{Ni}_3\text{Sn}_2$ HT	<i>hP6</i>	$\text{InNi}_2$	$P6_3/mmc$	...	...	[9]
$\text{Ni}_3\text{Sn}_2$ LT	<i>oP20</i>	$\text{Ni}_3\text{Sn}_2$	<i>Pnma</i>	...	$c^3d$	[9]
$\text{Ni}_3\text{Sn}_4$	<i>mC14</i>	$\text{Ni}_3\text{Sn}_4$	<i>C2/m</i>	...	$ai^3$	[9]
$\text{TiNi}_3$	<i>hP16</i>	$\text{TiNi}_3$	$P6_3/mmc$	...	adgh	[32]
TiNi	<i>cP2</i>	CsCl	<i>Pm3m</i>	B2	ab	[32]
$\text{Ti}_2\text{Ni}$	<i>cF96</i>	$\text{Ti}_2\text{Ni}$	<i>Fd3m</i>	...	cef	[32]

The purpose of the present work is to study the binary systems with the Ni content that will be available to used for thermodynamic optimization include in ternary systems containing Ni.

## 2. Method and modeling

The Gibbs energy ( ${}^0G_i^\phi$ ) of pure component *i* in phase  $\phi$  was expressed relative to the enthalpy of the component in its stable phase at 298.15 K.  $L_{ij}^\phi$  was a binary parameter describing the interaction between components *i* and *j* in phase  $\phi$ . For these parameters,  ${}^0G_i^\phi$  was a function of temperature and  $L_{ij}^\phi$  can be functions of temperature and composition.

Gibbs energy of formation of the binary compounds was expressed as:

$${}^0G_{A:B}^\phi = a {}^0G_A^\alpha + b {}^0G_B^\beta + A + B^*T \quad (1)$$

The solid binary phases belonging to the Ni–Sn and Ni–Ti binary systems were described with the respective sublattice models. Three phases were remodelled:  $\text{Ni}_3\text{Sn}_2$ \_LT,  $\text{Ni}_3\text{Sn}_4$  and NiTi.

## 3. Results and discussion

The thermodynamic description of the binary systems was presented in Table 2. The data marked with a reference code were taken from literature. Other parameters were optimized in this work and described with appropriate models.

Table 2 . The optimized parameters and models describing the phase relations of the Ni–Sn and Ni–Ti systems.

Phase	Model	Thermodynamic parameter	Ref.		
Liquid	(Ni,Sn,Ti)	${}^0L_{Ni:Sn}^L = -105002.87 + 197.9098T - 21.6959T \ln(T)$	[18]		
		${}^1L_{Ni:Sn}^L = -28342.17 + 52.5528T - 7.56094T \ln(T)$	[18]		
		${}^2L_{Ni:Sn}^L = 5582.31$	[18]		
		${}^0L_{Ni:Ti}^L = -153707.39 + 34.859449T$	[32]		
		${}^1L_{Ni:Ti}^L = -81824.775 + 25.809901T$	[32]		
Fcc	(Ni,Sn,Ti)(Va)	${}^0L_{Ni:Sn}^{Fcc} = -69460.28 + 79.2267T - 8.89084T \ln(T)$	[18]		
		${}^1L_{Ni:Sn}^{Fcc} = -8295.19$	[18]		
		${}^0T_{Ni:Sn}^{Fcc} = -6000$	[18]		
		${}^1T_{Ni:Sn}^{Fcc} = 3000$	[18]		
		${}^0L_{Ni:Ti}^{Fcc} = -130333.64 + 20.22423T$	[32]		
Bcc	(Ni,Ti)(Va)	${}^0L_{Ni:Ti}^{Bcc} = -97427.443 + 12.112037T$	[32]		
		${}^1L_{Ni:Ti}^{Bcc} = -32315.338$	[32]		
		${}^0L^{Hcp}_{Ni:Ti} = -20000$	[32]		
		$Ni_3Sn_2_{HT}$	(Ni)(Ni ,Sn) (Sn, Va)	${}^0G_{Ni_3Sn_2_{HT}}^{Ni:Ni:Sn} = -0.66667{}^0G_{Ni}^{Fcc} - 0.33333{}^0G_{Sn}^{Bct} - 22248.65 + 0.2828T$	[18]
				${}^0G_{Ni_3Sn_2_{HT}}^{Ni:Sn:Sn} = -0.33333{}^0G_{Ni}^{Fcc} - 0.66667{}^0G_{Sn}^{Bct} - 4935.38 + 7.5571T$	[18]
$Ni_3Sn_2_{LT}$	(Ni)(Ni ,Sn)(Sn, Va)	${}^0G_{Ni_3Sn_2_{LT}}^{Ni:Ni:Sn} = -0.8{}^0G_{Ni}^{Fcc} - 0.2{}^0G_{Sn}^{Bct} - 8256.41 + 8.4283T$	[18]		
		${}^0G_{Ni_3Sn_2_{LT}}^{Ni:Sn:Sn} = -0.4{}^0G_{Ni}^{Fcc} - 0.6{}^0G_{Sn}^{Bct} - 12287.83 + 6.0379T$	[18]		
		${}^0G_{Ni_3Sn_2_{LT}}^{Ni:Ni:Va} = -0.8{}^0G_{Ni}^{Fcc} = 13440.12 + 7.1312T$	[This work]		
		${}^0G_{Ni_3Sn_2_{LT}}^{Ni:Sn:Va} = -0.4{}^0G_{Ni}^{Fcc} - 0.4{}^0G_{Sn}^{Bct} = 13440.12 + 7.1312T$	[This work]		
		${}^0L_{Ni_3Sn_2_{LT}}^{Ni:Ni:Sn} = -78783.2$	[18]		
$Ni_3Sn_4$	(Ni,Ti)(Ni ,Sn) (Sn, Va)	${}^0G_{Ni_3Sn_4}^{Ni:Ni:Sn} = -0.45{}^0G_{Ni}^{Fcc} - 0.55{}^0G_{Sn}^{Bct} - 18172.44 + 10.18T$	[This work]		
		${}^0G_{Ni_3Sn_4}^{Ni:Sn:Sn} = -0.4{}^0G_{Ni}^{Fcc} - 0.6{}^0G_{Sn}^{Bct} - 18172.44 + 6.021T$	[This work]		
		${}^0G_{Ni_3Sn_4}^{Ni:Ni:Va} = -0.45{}^0G_{Ni}^{Fcc} = 9152.89$	[This work]		
		${}^0G_{Ni_3Sn_4}^{Ni:Sn:Va} = -0.4{}^0G_{Ni}^{Fcc} - 0.05{}^0G_{Sn}^{Bct} = 9152.89$	[This work]		
		${}^0L_{Ni_3Sn_4}^{Ni:Ni:Sn} = {}^0L_{Ni_3Sn_4}^{Ni:Ni:Sn:Va} = -41360.26$	[This work]		
$Ni_3Sn_{HT}$	(Ni,Sn)(Ni ,Sn)(Ni)	${}^0G_{Ni_3Sn_{HT}}^{Ni:Ni:Ni} = {}^0G_{Ni}^{Fcc} = 0$	[18]		
		${}^0G_{Ni_3Sn_{HT}}^{Sn:Ni:Ni} = -0.75{}^0G_{Ni}^{Fcc} - 0.25{}^0G_{Sn}^{Bct} = 13557.12 - 2.4434T$	[18]		
		${}^0G_{Ni_3Sn_{HT}}^{Ni:Sn:Ni} = -0.75{}^0G_{Ni}^{Fcc} - 0.25{}^0G_{Sn}^{Bct} = -21744.79 + 1.7049T$	[18]		
		${}^0G_{Ni_3Sn_{HT}}^{Sn:Sn:Ni} = -0.5{}^0G_{Ni}^{Fcc} - 0.5{}^0G_{Sn}^{Bct} = -24069.79 + 12.1937T$	[18]		
		${}^0L_{Ni_3Sn_{HT}}^{Ni:Sn:Ni} = {}^0L_{Ni_3Sn_{HT}}^{Ni:Sn:Sn:Ni} = -16726.09$	[18]		
$Ni_3Sn_{LT}$	(Ni)(Sn)	${}^0G_{Ni_3Sn_{LT}}^{Ni:Sn:Ni} = -0.75{}^0G_{Ni}^{Fcc} - 0.25{}^0G_{Sn}^{Bct} = -26882.47 + 5.9079T$	[18]		
		${}^0G_{NiTi}^{Ni:Ni} = {}^0G_{Ni}^{Bcc} = 0$	[This work]		
NiTi	(Ni, Ti, Va) (Ni, Ti, Va)	${}^0G_{NiTi}^{Ti:Ti} = 0$	[This work]		
		${}^0G_{NiTi}^{Va:Va} = 29000$	[This work]		
		${}^0G_{NiTi}^{Ti:Ni} = -0.5{}^0G_{Ni}^{Bcc} - 0.5{}^0G_{Ti}^{Bcc} = {}^0G_{NiTi}^{Ni:Ti} - 0.5{}^0G_{Ni}^{Bcc} - 0.5{}^0G_{Ti}^{Bcc} = -42472.1815 + 5.7654T$	[This work]		
		${}^0G_{NiTi}^{Ni:Va} = -0.5{}^0G_{Ni}^{Bcc} = {}^0G_{NiTi}^{Va:Ni} - 0.5{}^0G_{Ni}^{Bcc} = 61198 + 10T$	[This work]		
		${}^0L_{NiTi}^{Ni:Ni} = {}^0L_{NiTi}^{Ni:Ti} = 0$	[This work]		

		${}^0G_{Ti:Va}^{NiTi} = -0.5 {}^0G_{Ti}^{Bcc} = {}^0G_{Va:Ti}^{NiTi} = -0.5 {}^0G_{Ti}^{Bcc} = 49000 + 7T$ ${}^0L_{Ni, Va:Ti}^{NiTi} = {}^0L_{Ti, Ni:Va}^{NiTi} = -40000 + 17T$ ${}^0L_{Ni:Ti}^{NiTi} = {}^0L_{Va:Ni, Ti}^{NiTi} = -48000 + 20T$ ${}^0L_{Ti, Va:Ni}^{NiTi} = {}^0L_{Ni:Ti, Va}^{NiTi} = 23000 + 12T$	[This work] [This work] [This work] [This work]
Ni <sub>3</sub> Ti	(Ni,Ti) (Ni,Ti)	${}^0G_{Ni_3Ti}^{Ni_3Ti} = {}^0G_{Ni_3Ti}^{Hcp} = 0$ ${}^0G_{Ti_3Ni}^{Ni_3Ti} = {}^0G_{Ti_3Ni}^{Hcp} = 100$ ${}^0G_{Ni_3Ti}^{Ni_3Ti} = -0.75 {}^0G_{Ti_3Ni}^{Hcp} - 0.25 {}^0G_{Ni}^{Fcc} = -5688.27$ ${}^0G_{Ni_3Ti}^{Ni_3Ti} = -0.25 {}^0G_{Ti_3Ni}^{Hcp} - 0.75 {}^0G_{Ni}^{Fcc} = -41421.96 + 7.35868T$ ${}^0L_{Ni_3Ti}^{Ni_3Ti} = {}^0L_{Ti_3Ni}^{Ni_3Ti} = 18274.75 - 16.21228T$ ${}^0L_{Ni_3Ti}^{Ni_3Ti} = {}^0L_{Ti_3Ni}^{Ni_3Ti} = 50000$	[32] [32] [32] [32] [32]
NiT <sub>2</sub>	(Ni,Sn) (Ti)	${}^0G_{NiTi_2}^{NiTi_2} = -0.333 {}^0G_{Ni}^{Fcc} - 0.667 {}^0G_{Ti}^{Hcp} = -27514.2 + 2.85354T$ ${}^0G_{NiTi_2}^{NiTi_2} = -0.333 {}^0G_{Sn}^{Bct} - 0.667 {}^0G_{Ti}^{Hcp} = -36488.428 + 1.753T$	[32] [32]

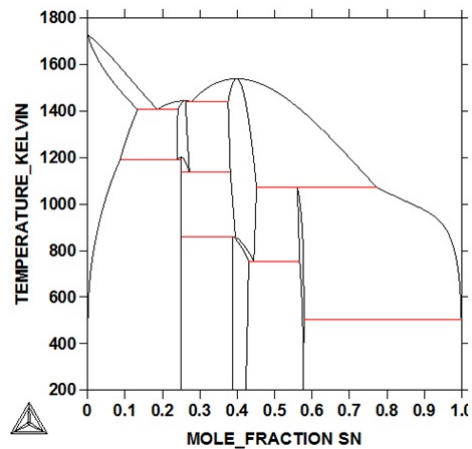
The one optimization of Ni–Sn system was done by Liu et al. [18].

The intermetallic phases in the system were described as: Ni<sub>3</sub>Sn<sub>HT</sub> - (Ni,Sn)<sub>0.25</sub>(Ni,Sn)<sub>0.25</sub>(Ni)<sub>0.5</sub>, Ni<sub>3</sub>Sn<sub>LT</sub> - (Ni)<sub>0.75</sub>(Sn)<sub>0.25</sub>, Ni<sub>3</sub>Sn<sub>2LT</sub> - (Sn)<sub>0.2</sub>(Ni,Sn)<sub>0.4</sub>(Ni)<sub>0.4</sub>, Ni<sub>3</sub>Sn<sub>2HT</sub> (Ni)<sub>0.3333</sub>(Ni,Sn)<sub>0.3334</sub>(Sn)<sub>0.3333</sub> and Ni<sub>3</sub>Sn<sub>4</sub> - (Ni)<sub>0.25</sub>(Ni,Sn)<sub>0.25</sub>(Sn)<sub>0.5</sub>. Optimization of authors [18] will be extrapolated in ternary Ni–Sn–Ti system with slight changing of models of phases Ni<sub>3</sub>Sn<sub>2LT</sub> and Ni<sub>3</sub>Sn<sub>4</sub>. Namely 3 sublattice models were used for them. Phase Ni<sub>3</sub>Sn<sub>2LT</sub> was modeled as (Ni)<sub>0.4</sub>(Ni,Sn)<sub>0.4</sub>(Sn, Va)<sub>0.2</sub> and Ni<sub>3</sub>Sn<sub>4</sub> as (Ni)<sub>0.4</sub>(Ni,Sn)<sub>0.05</sub>(Sn, Va)<sub>0.55</sub>.

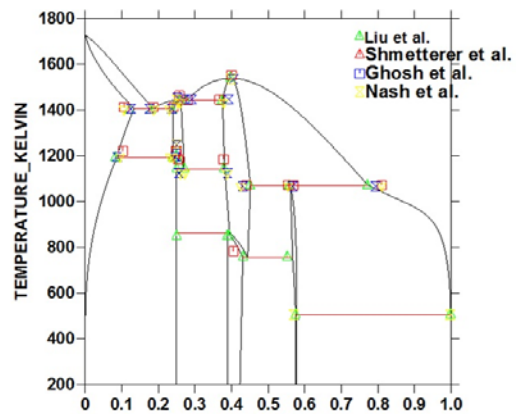
Fig. 1 presented Ni–Sn phase diagram. Fig. 1 a show diagram calculated with parameters obtained in this work. The phases Ni<sub>3</sub>Sn<sub>4</sub> and Ni<sub>3</sub>Sn<sub>2LT</sub> were remodelled using 3-sublattice model: (Ni)(Ni,Sn)(Sn, Va). In Fig. 1 b seen diagram compared with another results calculated and experimental found in literature. In the figure good correlation was observed in equilibrium point in diagram. Optimization of Tokunaga et al. [32] will be accepted in ternary Ni–Sn–Ti system too, but one phase only, intermediate phase NiTi was remodeled. In this work two sublattice symmetrical model (Ni,Ti, Va)<sub>0.5</sub>(Ni,Ti, Va)<sub>0.5</sub> was introduced for the phase.

Fig. 2 presented Ni–Ti phase diagram. Fig. 2 a show diagram calculated with parameters obtained in this work. In Fig. 2 b presented diagram compared with results calculated by Tokunaga et al. [32]. The equilibrium in NiTi diagram was keep. Narrow homogeneity region in NiTi phase was observed only compared with results [32].

Comparative revue in Fig. 3 was done between enthalpies of formation of all solid phases in two binary systems with AB-initio calculations and Thermocalc calculations. Good agreement was observed in obtained results.

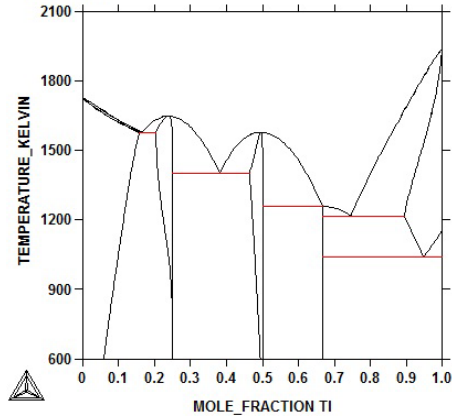


1 a)

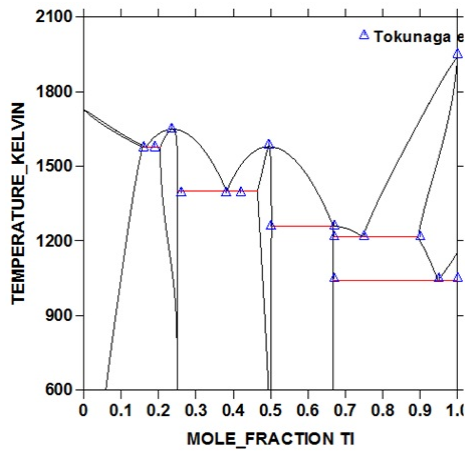


1 b)

Fig. 1. Calculated Ni–Sn phase diagram: a) this work, b) this work compared to experimental and calculated information.

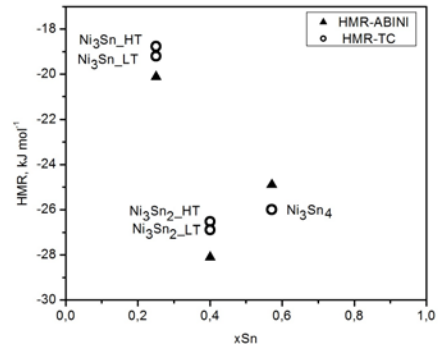


2 a)

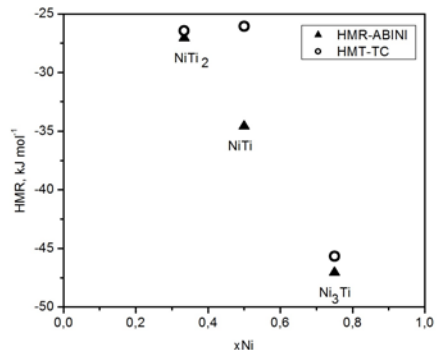


2 b)

Fig. 2. Calculated Ni–Ti phase diagram: a) this work, b) this work compared to coefficients of Tokunaga et al. [32].



3 a)



3 b)

Fig. 3. Comparative review of enthalpies of formation in solid phases of two binary systems calculated with AB - initio method and Calphad method.

Table 3 shows the calculated invariant points for two binary systems. The invariants calculated in this work compared by another taken from literature. All calculated temperatures appeared in close results.

Table 3. Calculated invariant points in this work, Liu et al. [18] and Tokunaga et al. [32] of the binary Ni–Sn and Ni–Ti systems.  $\phi$  – equilibrium phase.

$\phi_1 - \phi_2 - \phi_3$	Temp (°C)	$C_B^{\phi_1}$ (at%)	$C_B^{\phi_2}$ (at%)	$C_B^{\phi_3}$ (at%)	Ref.
Ni-Sn (at% Sn)					
$Ni_3Sn_2\_HT + Ni_3Sn\_LT = Ni_3Sn_2\_LT$	576	39.5	25.0	38.1	This work
	575	39.3	25.0	38.8	[18]
$Ni_3Sn_2\_HT = Ni_3Sn_2\_LT + Ni_3Sn_4$	481		43.1	56.6	This work
	483	44.4	43.2	55.2	[18]
$L + Ni_3Sn_2\_HT = Ni_3Sn_4$	796	76.9		56.1	This work
	796	77.1	45.0	55.7	[18]
Ni-Ti (at% Ti)					
$L = NiTi$	1310	49.4	49.4	-	This work
	1312	49.5	49.5	-	[32]
$Ni_3Ti = L + NiTi$	1120	24.3	38.2	46.4	This work
	1120	23.2	38.4	43.2	[32]
$NiTi = L + Ni_2Ti$	986	50.1	66.7	66.7	This work
	986	50.2	66.9	66.9	[32]

## 4. Conclusions

Two binary systems were modeled following the Calphad method. Obtained results are reasonable for starting point considering the include obtained results in another ternary systems. Three binary phases  $\text{Ni}_3\text{Sn}_2\text{-LT}$ ,  $\text{Ni}_3\text{Sn}_4$ ,  $\text{NiTi}$  were remodeled. Enthalpies of formation of all solid phases were calculated by two methods and good correlation was observed.

## References

- [1] K. Sukanuma, S-J. Kim, K-S. Kim, High-Temperature Lead-Free Solders: Properties and Possibilities, *JOM*, 2009, 61, pp. 64-71.
- [2] A. Dinsdale, A. Watson, A. Kroupa, J. Vrestal, A. Zemanova, J. Vizdal, Atlas of Phase Diagrams for the Lead-Free Soldering, COST 531 (Lead-free Solders), Vol. 1, © COST office, 2008, ISBN 978-80-86292-28-1, Printed in the Czech Republic.
- [3] A. Nash, P. Nash, Phase diagrams of binary nickel alloys, *Bull Alloy Phase Diag*, 67, 1985, 350-359.
- [4] T. B. Massalski, H. Okamoto, P. R. Subramanian, L. Kacprzak Binary alloy phase diagrams, ASM International, 1996.
- [5] D. Hanson, ES Sandford, H. Stevens, The Ni-Sn (Nickel-Tin) system, *J Inst Met*, 55, 1934, pp. 117-119.
- [6] W. Mikulas, L. Thomassen, Equilibrium Relations in the Ni-Sn System, *Trans AIME*, 124, 1937, pp. 111-137.
- [7] T. Heumann, The Equilibrium State in the Ni-Sn System, *Z Metallkd*, 35, 1943, pp. 206-211.
- [8] C. Schmetterer, H. Flandorfer, K. W. Richter, U. Saeed, M. Kauffman, P. Roussel, H. Ipsen, A new investigation of the system Ni-Sn, *Intermetallics*, 15, 2007, pp. 869-884.
- [9] A. Leineweber, M. Ellner, E.J. Mittemeijer, A NiAs/Ni<sub>2</sub>In-Type Phase  $\text{Ni}_{1+x}\text{Sn}$  ( $0.35 < x < 0.45$ ) with Incommensurate Occupational Ordering of Ni, *Journal of Solid State Chemistry*, 159, 2001, 191-197.
- [10] A. Leineweber, Variation of the crystal structures of incommensurate  $\text{LT}'\text{-Ni}_{1+\delta}\text{Sn}$  ( $\delta=0.35, 0.38, 0.41$ ) and commensurate  $\text{LT-Ni}_{1+\delta}\text{Sn}$  ( $\delta=0.47, 0.50$ ) with composition and annealing temperature, *Journal of Solid State Chemistry*, 177, 2004, pp. 1197-1212.
- [11] A. Leineweber, Journal of Solid State Chemistry, Incommensurately modulated  $\text{LT}'\text{-Ni}_{1+\delta}\text{Sn}$  ( $\delta=0.60, 0.63$ ): Rietveld refinement, line-broadening analysis and structural relation with  $\text{LT-}$  and  $\text{LT}'\text{-Ni}_{1+\delta}\text{Sn}$ , 182, 2009, pp. 1846-1855.
- [12] A. Leineweber, Development of compound layer during nitriding and nitrocarburising, *Int. J. Mat. Res. (formerly Z. Metallkd.)*, 102, 2011, pp. 861-873.
- [13] V. Glibin, T. Vorobyova, B. Kuznetsov, A comparative study of Ni-Sn solid and liquid alloys, *Thermochimica Acta*, 507, 2010, pp. 35-44.
- [14] R. Haddad, M. Gaune-Escard, J.P. Bros, A. Havlicek, E. Hayer, K.L. Komarek, Thermodynamics of nickel-tin liquid alloys, *J. Alloys Compounds*, 247, 1997, pp. 82-92.
- [15] H. Flandorfer, U. Saeed, C. Luef, A. Sabbar, H. Ipsen, Interfaces in lead-free solder alloys: Enthalpy of formation of binary Ag-Sn, Cu-Sn and Ni-Sn intermetallic compounds, *Thermochimica Acta*, 459, 2007, pp. 34-39.
- [16] G. Ghosh, Thermodynamic modeling of the nickel-lead-tin system, *Metall. Mater. Trans.*, 30A, 1999, pp. 1481-1494.
- [17] J. Miettinen, Thermodynamic description of the Cu-Ni-Sn system at the Cu-Ni side, *Calphad*, 27, 2003, pp. 309-318.
- [18] H.S. Liu, J. Wang, Z.P. Jin, Thermodynamic optimization of the Ni-Sn binary system, *Calphad*, 28, 2004, pp. 363-370.
- [19] A. Zemanova, A. Kroupa, A. Dinsdale, "Theoretical assessment of the Ni-Sn system" *Monatshefte für Chemie - Chemical Monthly*, 143, 9, 2012, pp. 1255-1261.
- [20] D. M. Poole and W. Hume-Rothery, The Equilibrium Diagram of the System Nickel-Titanium, *J. Inst. Metals*, 83, 1954-55, pp. 473-480.
- [21] K. Kajikawa, K. Oikawa, F. Takahashi, H. Yamada and K. Anzai, Reassessment of Liquid/Solid Equilibrium in Ni-Rich Side of Ni-Nb and Ni-Ti Systems, *Materials Transactions*, 51, 2010, pp. 781-786.
- [22] Y. Zhou, Q. Wang, D.L. Sun, X.L. Han, Co-effect of heat and direct current on growth of intermetallic layers at the interface of Ti-Ni diffusion couples, *Journal of Alloys and Compounds*, 509, 2011, pp. 1201-1205.
- [23] R. Luck and I. Arpshofen, Calorimetric determination of the enthalpies of formation of liquid Ni-Ti alloys = Détermination calorimétrique des enthalpies de formation des alliages liquides Ni-Ti, *Thermochimica Acta*, 131, 1988, pp. 171-181.
- [24] J. C. Gachon, M. Notin and J. Hertz, The enthalpy of mixing of the intermediate phases in the systems FeTi, CoTi, and NiTi by direct reaction calorimetry, *Thermochimica Acta*, 48, 1981, pp. 155-164.
- [25] J. C. Gachon and J. Hertz, Enthalpies of formation of binary phases in the systems FeTi, FeZr, CoTi, CoZr, NiTi, and NiZr, *Calphad*, 7 1, 1993, pp. 1-12.
- [26] J. L. Murray: P. Nash (Ed.), Phase Diagrams of Binary Nickel Alloys, ASM Int., 1991, pp. 342-355.
- [27] C. C. Jia, K. Ishida and T. Nishizawa: In: J. E. Morral, R. S. Schiffman and S. M. Merchant, editors. Experimental Methods of Phase Diagram Determination, Pub. TMS, Pittsburgh, PA, 1994, pp. 31-38.
- [28] L. Kaufman and H. Nesor, Computer Calculation of Phase Diagrams, *Calphad*, 2, 1978, pp. 81-108.
- [29] N. Saunders, Thermo Tech Ltd., Guilford: Unpublished work, 1992.
- [30] H. Liang and Z. Jin, A reassessment of the Ti-Ni system, *Calphad*, 17, 1993, pp. 415-426.
- [31] P. Bellen, K. C. H. Kumar and P. Wollants, Thermodynamic assessment of the Ni-Ti phase diagram, *Z. Metallkd.*, 87, 1996, pp. 972-978.
- [32] T. Tokunaga, K. Hashima, H. Ohtani and M. Hasebe, Thermodynamic Analysis of the Ni-Si-Ti System Using Thermochemical Properties Determined from Ab Initio Calculations, *Materials Transactions*, 45, 2004, pp. 1507-1514.
- [33] J. Keyzer, G. Cacciamani, N. Dupin, P. Wollants, Thermodynamic modeling and optimization of the Fe-Ni-Ti system, *Calphad*, 33, 2009, pp. 109-123.