Optimization of thermodynamic data
of the Ni–Si system ☆

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Abstract

The thermodynamic properties of the solid compound phases in the Ni–Si system were optimized by means of the non-linear Bayes algorithm. A consistent set of thermodynamic data consisting of the enthalpies and entropies of formations and the heat capacity functions is derived. The validity of the data is shown by computation of a well investigated chemical reaction. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Silicide of transition metals possess a large, application potential as high temperature materials with a high oxidation resistance [1] and as conducting paths in circuits [2]. The associated scientific interest is directed among other things towards the computation of phase equilibria and the reaction behavior. Fundamental precondition is the availability of reliable and precise thermodynamic data of the silicides.

The analysis of already existing data shows a considerable scatter for the enthalpies of formation [3]. The most comprehensive experimental investigation, including all nickel silicide phases, was performed by

Oelsen [4,5]. Individual nickel silicide phases were investigated by several authors [6,7]. Regarding the entropies of formation or the standard entropies of the silicides, less experimental values are available [10–12].

The optimization of the thermodynamic data of the system nickel–silicon is the subject of two earlier works of Chart [8] and Mey [9]. Both works are based mainly on the experimental results cited above. The only complete set of enthalpies and entropies of formation of the nickel silicides is given by the optimization of Mey [9].

The aim of this work is a critical assessment of the available thermodynamic data of the silicides $NiSi_2$, $NiSi$, Ni_3Si_2, Ni_2Si and Ni_5Si_2. The calculations are based on a data set, which was derived from different independent experimental results, e.g. calorimetric measurements, EMF measurements, and from the established Ni–Si phasediagram [13]. As tool for the computation the program system ChemSage is used [14].

One criterion for the quality of the modelled data is e.g. the correct rendition of the experimentally determined phase diagram. But, this demand can be fulfilled mathematically with different data sets. Therefore, the correct computation of a well examined chemical reaction is introduced here as an additional criterion.

2. Method of calculation

The pure elements Si and Ni, as well as the stoichiometric compound phases are described by the conventional Gibbs energy function, Eq. (1),

$$G(T) = \Delta_F H(T) - T \cdot S^0(T), \qquad (1)$$

where $\Delta_F H$ denotes the enthalpy of formation and S^0 the standard entropy. The conventions are $\Delta_F H$ (298.15 K, *elements*) = 0 and S^0 (0 K) = 0.

The conventional Gibbs energy function is represented by an equation with fixed coefficients, Eq. (2).

$$G(T) = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1}. \qquad (2)$$

All calculations were carried out with the program ChemSage [14]. This program employs the minimization of the Gibbs energy of the system by taking into account of the global parameters system composition, temperature and total pressure. For the assessment of the Ni–Si phase diagram the optimizer module is used. A nonlinear least-squares procedure, the Bayes estimation procedure, performs the estimation of model parameters from experimental data. The main advantage of this procedure is, that additional a priori parameters from independent measurements or theoretical considerations are involved. Whereas the conventional weighted least-square algorithm takes only experimental data into account [15–17].

The basis for the calculation of molar standard enthalpies of formation is briefly discussed in the simple case of a congruently melting compound. The melting point of a compound is the point of intersection of the Gibbs energy function of the liquid phase with the Gibbs energy function of the solid phase at constant pressure and constant composition. If the melting point and the Gibbs energy function of the melt at given composition are known, then the

Gibbs energy function of the solid phase on the basis of experimental data can be varied in such a way, that the point of intersection with the Gibbs energy function of the melt results in the known melting point. The optimization routine varies the unknown quantities in the Gibbs energy function of the solid phase (e.g. the enthalpy of formation, the standard entropy or the heat capacity function), such that the point of intersection with the Gibbs energy function of the melt results in the melting point of the compound. For more complex systems, e.g. modelling of incongruently melting compound, the mass balance has to be considered.

3. The data set of the liquid phase

The data set of the liquid phase is based on EMF measurements of nickel–silicon melts in the temperature range between 1480°C and 1610°C [18]. Because of the scatter of the experimental data at high silicon contents ($x_{Si} > 0.5$), the activity coefficients of silicon γ_{Si} were calculated from the silicon–liquidus curve of the nickel–silicon phase diagram (Fig. 1) [13]. This calculation was based on the heat of fusion of pure silicon [19] and on the partial heats of mixing $\Delta_M H_{Si}$ of silicon in the nickel–silicon melt as estimated from the integral heats of mixing [4].

After computation of the coefficients of activity for nickel by the Gibbs–Duhem relationship the molar Gibbs excess energy of mixing after Eq. (3) was calculated.

$$\Delta G^{ex} = RT(x_{Si}\ln\gamma_{Si} + x_{Ni}\ln\gamma_{Ni}). \qquad (3)$$

The molar Gibbs excess energy is described as function of the mole fraction of silicon with a Redlich–Kister polynomial with four coefficients of interaction (Eq. (4)).

$$\Delta G^{ex}(T, x_{Si}) = x_{Si}(1 - x_{Si})$$
$$\times [L^0_{ij} + L^1_{ij}(2x_{Si} - 1) + L^2_{ij}(2x_{Si} - 1)^2$$
$$+ L^3_{ij}(2x_{Si} - 1)^3], \qquad (4)$$

(L^ν_{ij}, coefficient of interaction, i = Si, j = Ni, ν = 0, 1, 2, 3 (order of the interaction)). The coefficients were determined by least-square fitting. The temperature dependence of the molar Gibbs excess energy is expressed by the temperature dependence of the coef-
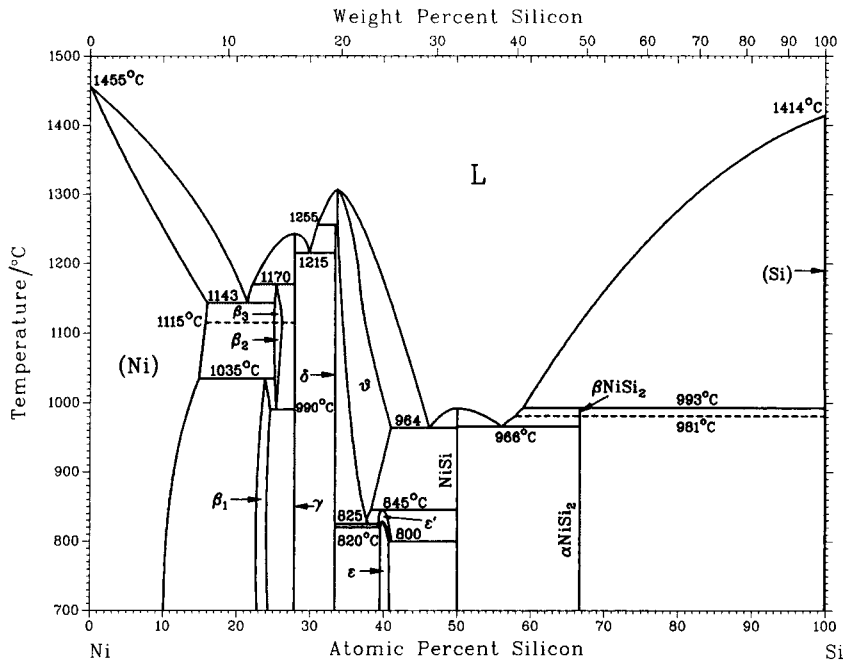
Fig. 1. The nickel–silicon phase diagram (reprinted from [13], Copyright 1986 ASM International).

ficients of interaction (Eq. (5)), which are listed in Table 3.

$$L_{ij}^v = A_{ij}^v + B_{ij}^v T. \tag{5}$$

Eq. (5) is equivalent to Eq. (6).

$$\Delta G^{\text{ex}} = \Delta_{\text{mix}} H - T S^{\text{ex}}. \tag{6}$$

With standard enthalpies of the liquid elements $G_{\text{Si}}{}^\circ$ and $G_{\text{Ni}}{}^\circ$ [19] a complete data set of the molar Gibbs energy of the nickel–silicon melt results (Eq. (7)).

$$
\begin{aligned}
G(\text{liquid}, T) =\ & x_{\text{Si}} G_{\text{Si}}{}^\circ + x_{\text{Ni}} G_{\text{Ni}}{}^\circ \\
& + RT[x_{\text{Si}} \ln x_{\text{Si}} + x_{\text{Ni}} \ln x_{\text{Ni}}] \\
& + \Delta G^{\text{ex}}(T, x_{\text{Si}}). \tag{7}
\end{aligned}
$$

In Fig. 2 the good agreement between the calculated molar enthalpy of mixing with the experimental determined values of Stukalo [20], Witusiewicz [21] and the assessed values of Chart [8] at 1873 K is shown. It has to be pointed out, that our model is based on a temperature independent molar enthalpy of mixing. Fig. 3 compares the calculated molar entropies of mixing with experimental results of Stukalo [20] and with the assessed values of Chart [8]. Here,
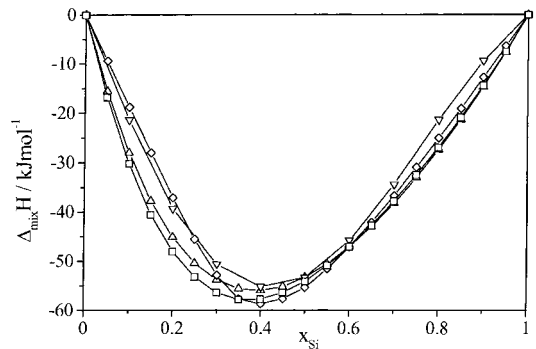

Fig. 2. Molar enthalpy of mixing of nickel and silicon at 1873 K: (∇) Ref. [20]; ($\diamondsuit$) Ref. [8]; ($\triangle$) Ref. [21]; ($\square$)optimized values (this work).

significant differences mainly in the shape of the curve, but also in the values are evident.

4. The data L_{ij}^v set of the solid compound phases

In the Ni–Si system there are a number of compounds with a small homogenity range, which were treated as being stoichiometric compounds (Fig. 1).
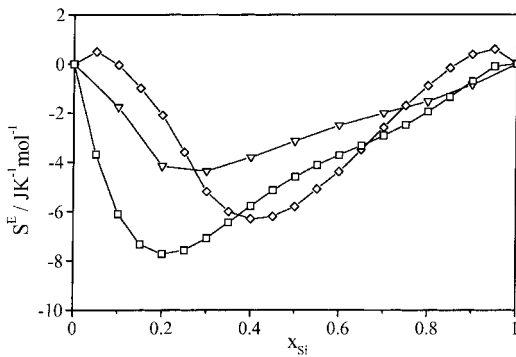
Fig. 3. Molar entropy of mixing of nickel and silicon at 1873 K: (∇) Ref. [20]; ($\diamond$) Ref. [8]; ($\square$)optimized values (this work).

The most important source of experimental data is the established Ni–Si phase diagram [13]. All melting points, transition temperatures, temperatures and compositions of liquidus curves were obtained from this diagram (Fig. 1). Further sources are the available, experimentally determined thermodynamic data in literature [4–12,22–24], listed in the Tables 1–4. As starting values for the calculation the enthalpies of formations determined by Oelsen [4,5] have been set. Estimations for missing heat capacity functions were based on the Neumann–Kopp rule.

Starting point of the optimization was the congruently melting compound Ni–Si. The thermodynamic properties of a single-crystal of Ni–Si have been recently investigated, and the heat capacity function

between 10 and 400 K, the standard entropy function and the standard entropy of formation determined [12]. As described in chapter 2, the enthalpy of formation was calculated with respect to the phase equilibrium at the melting point of 1265 K. The same procedure was chosen for the calculation of the Ni_2Si phase. The neighbouring phases of NiSi and Ni_2Si in the phase diagram were calculated with respect to the Gibbs energy function of NiSi and Ni_2Si. The high temperature phases of Ni_3Si, Ni_3Si (β_2) and Ni_3Si (β_3) are not considered, as well as the Ni–Si mixed phase.

5. Results

The results of the optimization procedure, the enthalpies and entropies of formation, the melting points and the enthalpies of fusion are shown in Table 5. All values (enthalpies, entropies, and heat capacities) are referred to 1 mol stoichiometric compound phase with the general formula Ni_xSi_{1-x}. The

Table 3
The coefficients of interaction A_{ij}^ν and B_{ij}^ν of the (nickel + silicon) melt (Eq. (2))

ν	A_{ij}^ν (J mol^{-1})	$10^3 B_{ij}^\nu$ (J K^{-1} mol^{-1})
0	−216366	41.468
1	−111219	20.356
2	−491023	41.203
3	2916.44	26.772

Table 1
Molar enthalpies of formation of the nickel silicides (KJ mol^{-1})

Reference	Ni$_3$Si	Ni$_5$Si$_2$	Ni$_2$Si	Ni$_3$Si$_2$	NiSi	NiSi$_2$
[4,5]	−37.2	−42.3	−46.9	−45.2	−43.1	−29.3
[6]					−42.4 ± 0.9	
[7]		−45.1 ± 1.4	−50.6 ± 1.7			
[8] (calculated.)	−35.6 ± 4	−42.3 ± 4	−47.7 ± 4	−46.6 ± 4	−44.8 ± 4	−31.4 ± 4
[9] (calculated.)	−41.2	−41.3	−37.6	−37.0	−33.9	−27.3

Table 2
Molar entropies of formation of the nickel silicides (J K^{-1} mol^{-1})

Reference	Ni$_3$Si	Ni$_5$Si$_2$	Ni$_2$Si	Ni$_3$Si$_2$	NiSi	NiSi$_2$
[10]					−2.1 ± 1.5	
[11]						−0.7 ± 1.5
[12]					−0.54 ± 0.04	
[9] (calculated.)	−10.3	−8.1	−4.4	−5.0	−4.3	−6.0

Table 4
Thermodynamic values of nickel silicides

Phase	Temperature of melting or decomposition (K)	$C_p(T)$ (J K^{-1} mol^{-1})	$\Delta_{\text{fus}}H$ (KJ mol^{-1})
Ni$_3$Si (β_1)	1308	–	–
Ni$_5$Si$_2$	1515	–	–
Ni$_2$Si	1579	$20.54 + 9.05 \times 10^{-3}T - 8.45\,10^4 T^{-2}$ (400–1580 K) [22]	18.1 [6]
Ni$_3$Si$_2$	1118		
NiSi	1265	$21.61 + 1.07 \cdot 10^{-2}T - 1.815 \times 10^5 T^{-2}$ (373–1260 K) [24]; 22.77 ± 0.02 [12]; $15.14 + 2.82 \times 10^{-2}T - 8.752 \times 10^4 T^{-2}$ (123–323 K) [23]	20.7 [6]; 21.5 [24]
NiSi$_2$	1266	$25.026 + 3.686 \cdot 10^{-3}T - 3.611 \times 10^5 T^{-2}$ (373–1260 K) [10]; 22.05 [11]	

Table 5
Results of the optimization procedure, enthalpies (KJ mol^{-1}) and entropies (J K^{-1} mol^{-1}) of formation

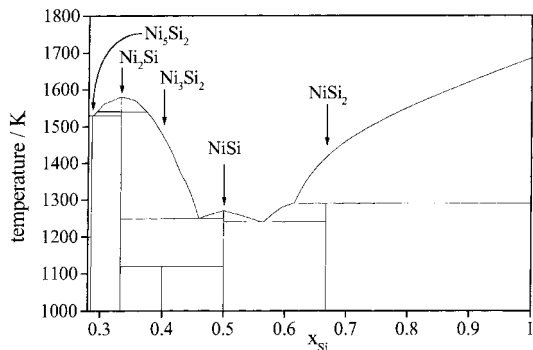| Phase	x_{Si}	$\Delta_B H$ (KJ mol^{-1})	$\Delta_B S$ (J K^{-1} mol^{-1})	Temperature of melting or decomposition (K)	$\Delta_{\text{fus}}H$ (KJ mol^{-1})
Ni$_3$Si (β_1)	0.238	−39.37	−0.45	1308	–
Ni$_5$Si$_2$	0.286	−42.40	−0.30	1526	11.63
Ni$_2$Si	0.333	−47.70	−0.08	1577	19.21
Ni$_3$Si$_2$	0.4	−46.04	−0.95	1118	–
NiSi	0.5	−42.40	-0.54 ± 0.04[a]	1270	23.18
NiSi$_2$	0.667	−28.87	−0.51	1279	–

[a] Experimental [12].

Fig. 4. The calculated Ni–Si phase diagram.

enthalpies of formation agree satisfactorily with the experimental determined values of Oelsen [4]. The entropies of formation are slightly negative and are in the order of experimental values [10,12]. The phase diagram calculated (Figs. 4 and 5) with this values agrees very good with the established Ni–Si phase diagram (Fig. 1). In Table 6 the coefficients of the heat capacity functions of the solid compound phases are summarized.

For the reliability of calculated thermodynamic values, the rendition of the phase diagram is a necessary but not sufficient condition. The quality of the data has to be proved by an independent way. Here, the calculation of a well examined reaction is suggested.

$$\text{Ni} + z\text{SiCl}_4 + z\text{H}_2 \Leftrightarrow \text{NiSi}_x + (z-x)\text{HSiCl}_3 + x\text{HCl} \tag{8}$$
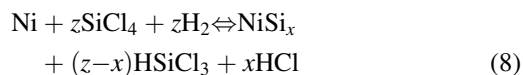
Nickel reacts with gaseous silicontetrachloride and hydrogen to a nickel silicide phase NiSi$_x$, trichlorosilane and hydrogen chloride. This reaction has a number of advantages for verifying of thermodynamic relations: a very high reaction rate, the thermodynamic equilibrium is reached in a very short time, the results are highly reproducible and reversible, the solid and gaseous products are quantitatively analyzed [25]. The process is performed in a highly sophisticated flow-reactor, the products were determined and quantified by on-line gas chromatography. Depending on the chosen temperature, nickel silicides with different silicon content can be obtained [25]. The nickel silicide phases, which are formed with increasing temperature in the course of reaction (8), have been
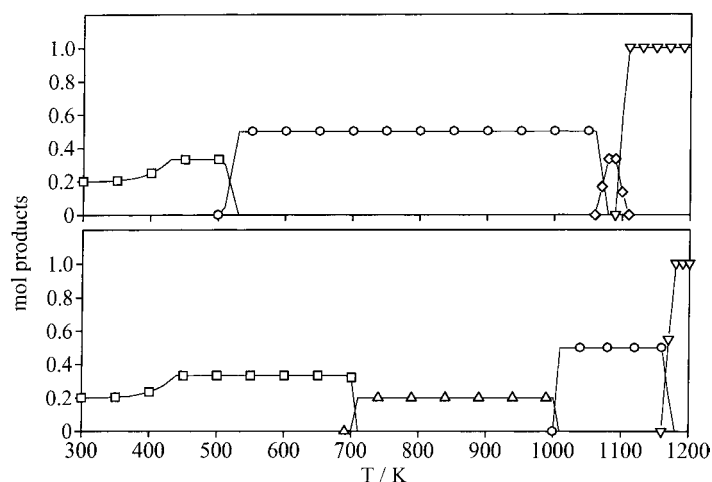
Fig. 5. Calculated nickel silicide phase sequence of reaction (8) with data from [9] (lower figure), and data of this work (upper figure), ($\square$) NiSi; (Δ) Ni_5Si_2; (o) Ni_2Si; ($\Diamond$) Ni_3Si_2; (∇) NiSi.

Table 6
Results of the optimization procedure, coefficients of the heat capacity functions of the silicides, $C_p(T) = a + bT + cT^2 + dT^{-2}$ (J K^{-1} mol^{-1})

Phase	x_{Si}	a	b	c	d
Ni_3Si	0.25	24.81	5.14×10^{-3}	0	-103554
Ni_5Si_2	0.286	21.65	1.09×10^{-2}	0	0
Ni_2Si (low)	0.333	21.41	8.13×10^{-3}	0	0
Ni_2Si (high)	0.333	21.41	8.13×10^{-3}	0	0
Ni_3Si_2	0.4	24.54	4.44×10^{-3}	0	-232003
NiSi	0.5	20.23	1.02×10^{-2}	3.25×10^{-6}	0
$NiSi_2$	0.667	25.02	3.68×10^{-3}	0	-361233

calculated with the data set of Mey [9] and with the optimized values from this work. For the calculation an excess of $SiCl_4$ and H_2 of 100 times with respect to Ni had been chosen. In Fig. 5 both results are compared. With the thermodynamic data, obtained by the optimization presented in this work, the experimental found sequence of silicide formation is fully described. Whereas the data given in [9] does not allow a satisfying description of the reaction (8).

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