

SIMPLIFICATION OF THE THERMODYNAMIC DESCRIPTION OF THE Ti-Si SYSTEM

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Abstract

The thermodynamic optimization of ternary or higher order systems containing Ti requires that the Ti-X binary systems are continuously updated. The Ti-Si system has been studied and thermodynamically optimized since de 1950s. The Ti_5Si_3 phase was initially considered stoichiometric to facilitate the thermodynamic calculations, although experimental results showed that this phase was a non-stoichiometric intermetallic. The most recent optimization of the Ti-Si system described this phase as a non-stoichiometric intermetallic with three sublattices, using the sub-lattice model. The problem of this approach is that it increases considerably the number of variables to be optimized during the calculation of the Ti-Si-X phase diagrams, hindering the convergence of the computational processing. The present work simplifies the optimization of the Ti-Si system, assuming that Ti_5Si_3 phase is mostly hyper-stoichiometric in relation to Ti. The results showed that this simplification did not significantly affect the phase diagram and the thermodynamic properties calculated for the system.

Keywords: Ti-Si; Thermodynamic optimization; Thermo-calc; Parrot.

SIMPLIFICAÇÃO DA DESCRIÇÃO TERMODINÂMICA DO SISTEMA Ti-Si

Resumo

A otimização termodinâmica de sistemas ternários ou de maior ordem contendo Ti necessita que os sistemas binários Ti-X estejam sempre atualizados. O sistema Ti-Si já foi amplamente estudado e otimizado termodinamicamente. Um dos seus compostos intermediários, a fase Ti_5Si_3 , foi inicialmente considerada como sendo estequiométrica de modo a facilitar o processo de otimização de variáveis de funções termodinâmicas, embora os resultados experimentais confirmassem a sua não estequiométrica. A otimização mais recente modelou esta fase como sendo não-estequiométrica com três sub-redes. O problema dessa abordagem é que ela pode aumentar significativamente o número de variáveis a serem otimizadas no cálculo de sistemas ternários Ti-Si-X, dificultando a convergência do processamento computacional. O presente trabalho simplifica a otimização do sistema Ti-Si, considerando que a fase Ti_5Si_3 é sempre hiper-estequiométrica em relação ao Ti. Os resultados mostraram que esta simplificação não afetou significativamente o diagrama de fases e os valores das propriedades termodinâmicas do sistema.

Palavras-chave: Ti-Si; Otimização termodinâmica; Thermo-calc; Parrot.

1 INTRODUCTION

The interest on the Ti-Si system is fundamentally related to the beneficial effects of Si on high temperature properties of Ti-X-Al alloys, such as creep and oxidation resistance [1-3]. Hansen [4] experimentally investigated the Ti-Si phase diagram in the 50s and they showed the presence of non-stoichiometric Ti_5Si_3 phase and indicated the presence of an eutectoid reaction, represented by $Ti(\beta) \rightarrow Ti(\alpha) + Ti_5Si_3$. Almost 20 years later, Svechnikov et al. [5] presented a new

experimental version of the Ti-Si system, showing the presence of a peritectoid reaction, represented by $Ti(\beta) + Ti_5Si_3 \rightarrow Ti_3Si$; and an eutectoid reaction, represented by $Ti(\beta) \rightarrow Ti(\alpha) + Ti_3Si$. The first thermodynamic optimization of the system was performed by Kaufman [6], which used the experimental results of Hansen [4] (without the presence of Ti_3Si and Ti_5Si_4 phases), but considering the Ti_5Si_3 phase as stoichiometric. Vahlas et al. [7] conducted a thermodynamic optimization

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based on data from Svechnikov et al. [5], but considering the Ti_5Si_3 phase as stoichiometric. Only in the mid-90s that Seifert et al. [8] performed a thermodynamic optimization of the Ti-Si system, which were more consistent with previous experimental results [4-5]. The variables calculated in this optimization were incorporated into the thermodynamic databases of computational thermodynamic software. The major distinction of the thermodynamic modeling made by Seifert et al. [8] was to consider the non-stoichiometric intermetallic Ti_5Si_3 phase with three sublattices, with a configuration represented by $(Ti,Si)_2(Si,Ti)_3(Ti)_3$. Most intermediate phases of the Si-X systems are, however, hyper-stoichiometric with respect to the element X [9] such as Y_5Si_3 and V_3Si phases.

The ternary system Ti-Al-Si was investigated experimentally by Crossley et al. [10] Crossley and Turner [11], Schob et al. [12], Wu et al. [13], Azevedo [1], Azevedo and Flower [2, 14], Bulanova et al. [15] and Perrot [16]. All these investigations showed that Al was soluble in non-stoichiometric Ti_5Si_3 phase. This ternary system was thermodynamically optimized by Azevedo [1] and Azevedo and Flower [2,3], assuming, however, that the Ti_5Si_3 phase was stoichiometric and without Al solubility. For the future thermodynamic optimization of the ternary Ti-Al-Si system with the presence of non-stoichiometric Ti_5Si_3 phase with Al solubility, a better description of this phase should be used. The description of Ti_5Si_3 phase with 3 sublattices as proposed by Seifert et al. [8] would lead to the use of eight hypothetical phases and at least 40 missing interaction parameters, which could hinder the convergence of the optimization procedure during the calculation of these parameters.

The objective of this paper is to simplify the optimization of Ti-Si system using 3 sublattices but assuming that Ti occupies the Si sublattice in the following description: $(Ti)_2(Si,Ti)_3(Ti)_3$. The number of variables to be optimized for the calculation of the Ti-Si and Ti-Al-Si systems would decrease considerably, simplifying the thermodynamic optimization of the ternary Ti-Al-Si phase diagram.

2 MATERIALS E METHODS

The invariant equilibria considered in present thermodynamic optimization are presented in Table I and the enthalpies of formation of intermediate phases are shown in Table 2.

The liquid and solid solutions have been described thermodynamically using the model of substitutional solution [21]. Thus (Equations 1-4):

$$G^{phase} = {}^{ref}G + {}^{id}G + {}^{exc}G \quad (1)$$

$${}^{ref}G^{phase} = X_{Si} {}^{ref}G_{Si} + X_{Ti} {}^{ref}G_{Ti} \quad (2)$$

Where: ${}^{ref}G_i = {}^{SER}G_i$

$${}^{id}G^{phase} = R \cdot T [X_{Si} \cdot \ln X_{Si} + X_{Ti} \cdot \ln X_{Ti}] \quad (3)$$

$${}^{exc}G^{phase} = X_{Si} \cdot X_{Ti} \cdot L^{phase} \quad (4)$$

The interaction parameter was described by a Redlich-Kister polynomial (see Equations 5 and 6).

$$L^{phase} = {}^0L^{phase} + {}^1L^{phase} (X_{Si} - X_{Ti}) + \dots + {}^vL^{phase} (X_{Si} - X_{Ti})^v \quad (5)$$

Where:

$${}^vL^{phase} = a + bT + \dots \quad (6)$$

For the description of the Ti_5Si_3 phase, the sublattice model (Compound Energy Formalism [25]) was used, with the following sublattice configuration: $(Ti)_2(Si,Ti)_3(Ti)_3$ (Equations 7 and 8).

$$G^{Ti_5Si_3} = y_{Si}'' \cdot {}^{Ref}G_{Ti:Si:Ti}^{Ti_5Si_3} + y_{Ti}'' \cdot {}^{Ref}G_{Ti:Ti:Ti}^{Ti_5Si_3} + 3 \cdot R \cdot T [y_{Si}'' \cdot \ln(y_{Si}'') + y_{Ti}'' \cdot \ln(y_{Ti}'')] + {}^{Exc}G^{Ti_5Si_3} \quad (7)$$

$${}^{Exc}G^{Ti_5Si_3} = y_{Ti}' \cdot y_{Ti}'' \cdot y_{Si}'' \cdot y_{Ti}''' \cdot L_{Ti:Si,Ti:Ti} = y_{Ti}'' \cdot y_{Si}'' \cdot L_{Ti:Si,Ti:Ti} \quad (8)$$

Where: y is the site fraction in the sublattice and the superscripts ‘, ’ and ‘’’ refer to the 1st, 2nd and 3rd sublattices of the compound, respectively. As in the 1st and 3rd sublattices there is only Ti, the sites fraction of Ti in them are equal to one.

The free energies for the formation of the end-members, ${}^{ref}G_{Ti:Ti:Ti}^{Ti_5Si_3}$ and ${}^{ref}G_{Ti:Si:Ti}^{Ti_5Si_3}$, were considered to be the same as the ones calculated by Seifert et al. [8]. For the description of the stoichiometric intermediate phases, the Kopp-Neumann rule was used resulting in the following equation for a Ti_mSi_n phase (Equation 9) [25]:

Table I. Invariant equilibria for the system Ti-Si [4-5] considered in present work

Equilibrium	Reaction	T(K)	100.X _{Si}
L ↔ Ti ₅ Si ₃	Congruent melting	2403	37.5
L ↔ TiSi ₂	Congruent melting	1773	66.66
L ↔ Ti(β) + Ti ₅ Si ₃	Eutectic	1613	13.7
L ↔ TiSi ₂ + Si	Eutectic	1603	86
L ↔ TiSi + TiSi ₂	Eutectic	1743	64.1
L + Ti ₅ Si ₃ ↔ Ti ₅ Si ₄	Peritectic	2193	48
L + Ti ₅ Si ₄ ↔ TiSi	Peritectic	1843	60
Ti(β) + Ti ₅ Si ₃ ↔ Ti ₃ Si	Peritectoid	1443	25
Ti(β) ↔ Ti(α) + Ti ₃ Si	Eutectoid	1133	1.1

X_{Si} = Atom fraction of Si.

$$G^{\text{phase}} = m \cdot G_{\text{Ti}}^{\text{SER}} + n \cdot G_{\text{Si}}^{\text{SER}} + c + d \cdot T \quad (9)$$

The thermodynamic parameters used in the present study are listed in Table 3. The parameters of GHSER were obtained from SGTE data [26]. Data were optimized using the CALPHAD technique with the help of the Parrot module of Thermo-calc.

3 RESULTS E DISCUSSION

The optimization for the calculation of the ${}^0L_{\text{Ti};\text{Ti},\text{Si};\text{Ti}}^{\text{Ti}_5\text{Si}_3}$ interaction parameters resulted in the coefficients **a = +1.74102703E+05 (J/mol)** and **b = -9.77215453E+01 (J/mol.K)**. The results of invariant equilibria are shown in Table 4, indicating that the calculated values are very

Table 2. Enthalpies of formation at 298.15K of intermediate phases of Ti-Si system (kJ/mol of atoms)

Type	Ti ₃ Si ₂	Ti ₅ Si ₄	TiSi	TiSi ₂	Ti ₃ Si	Ref
C	-72.67	-79	-77.76	-57.036	-50	Seifert et al. [8]
E	-73.8	-78.5	-72.6			Meschel and Kleppa [17]
E	-78.1	-75.9	-71.5	-53.5		Kematch and Myers [18]
A	-72.53	-74.63	-72.23		-47.11	Colinet and Tedenac [19]
E				-55	-48	Coelho et al. [20]
E				-56.97		Topor and Kleppa [21]
E	-72.42					Maslov et al. [22]
E	-72.52					Robins and Jenkins [23]
E	-72.383		-64.852	-44.769		Engqvist et al. [24]

C=calculated; E=experimental; A=ab initio.

Table 3. Thermodynamic parameters used in the present work (J/mol) [8]

Phase	Parameter	Equation
Liquid	${}^0L_{\text{Ti};\text{Si}}^{\text{liq}}$	255852.17 + 21.87411*T
	${}^1L_{\text{Ti};\text{Si}}^{\text{liq}}$	25025.35 - 2.00203*T
	${}^2L_{\text{Ti};\text{Si}}^{\text{liq}}$	83940.65 - 6.71526*T
Ti(α)	${}^0L_{\text{Ti};\text{Si};\text{Va}}^{\text{Ti}(\alpha)}$	-302731.04 + 69.08469*T
	${}^1L_{\text{Ti};\text{Si};\text{Va}}^{\text{Ti}(\alpha)}$	+25025.35 - 2.00203*T
	${}^2L_{\text{Ti};\text{Si};\text{Va}}^{\text{Ti}(\alpha)}$	+83940.65 - 6.71526*T
Ti(β)	${}^0L_{\text{Ti};\text{Si};\text{Va}}^{\text{Ti}(\beta)}$	-275629.1 + 42.5094*T
	${}^1L_{\text{Ti};\text{Si};\text{Va}}^{\text{Ti}(\beta)}$	+25025.35 - 2.00203*T
	${}^2L_{\text{Ti};\text{Si};\text{Va}}^{\text{BCC}}$	+83940.65 - 6.71526*T
Diamond - Si	${}^0L_{\text{Ti};\text{Si}}^{\text{Diam}}$	80*T
Ti ₃ Si	${}^0G_{\text{Ti};\text{Si}}^{\text{Ti}_3\text{Si}}$	-200000 + 3.19924*T + GHSESI + 3*GHSERTI
Ti ₅ Si ₄	${}^0G_{\text{Ti};\text{Si}}^{\text{Ti}_5\text{Si}_4}$	-711000 + 22.37355*T + 4*GHSESI + 5*GHSERTI
TiSi	${}^0G_{\text{Ti};\text{Si}}^{\text{TiSi}}$	-155061.7 + 7.6345*T + GHSESI + GHSERTI
TiSi ₂	${}^0G_{\text{Ti};\text{Si}}^{\text{TiSi}_2}$	-175038.5 + 4.548*T + GHSERTI + 2*GHSESI
Ti ₅ Si ₃	${}^0G_{\text{Ti};\text{Si};\text{Ti}}^{\text{Ti}_5\text{Si}_3}$	-583564.31 + 2.68514*T + 5*GHSERTI + 3*GHSESI
	${}^0G_{\text{Ti};\text{Ti};\text{Ti}}^{\text{Ti}_5\text{Si}_3}$	+40000 + 20*T + 8*GHSERTI
	${}^0L_{\text{Ti};\text{Ti},\text{Si};\text{Ti}}^{\text{Ti}_5\text{Si}_3}$	a + b*T †

†: a=J/mol of phase; b=J/(mol of phase).K.

Table 4. Calculated invariant equilibria of the Ti-Si system

Reaction	Calculated	Difference (experimental – calculated)	Difference* %	
L=Ti ₅ Si ₃	T(K)	2391	-11.71	0.5
	X _{Si}	0.374	-9.9E-4	0.3
L=TiSi ₂	T(K)	1757	-15.78	0.9
	X _{Si}	0.6667	6.7E-3	1.0
L=Ti(β) + Ti ₅ Si ₃	T(K)	1618	4.84	0.3
	X _{Si} ^L	0.1296	-7.4E-3	6.1
	X _{Si} ^β	4.70E-2	4E-5	0.1
	X _{Si} ^{Ti₅Si₃}	0.3434	1.8E-2	5.0
L=TiSi ₂ + Si	T(K)	1604	1.27	0.1
	X _{Si} ^L	0.8149	-4.5E-2	5.8
	X _{Si} ^{TiSi₂}	0.6667	6.7E-5	0.0
	X _{Si} ^{Si}	1	-3.5E-11	0.0
L=TiSi ₂ + TiSi	T(K)	1747	4.4	0.3
	X _{Si} ^L	0.6365	-4.5E-3	0.7
	X _{Si} ^{TiSi}	0.5	0	0.0
	X _{Si} ^{TiSi₂}	0.6667	6.7E-5	0.0
L + Ti ₅ Si ₃ =Ti ₅ Si ₄	T(K)	2213	-20.05	0.9
	X _{Si} ^L	0.4727	-3.8E-3	0.8
	X _{Si} ^{Ti₅Si₃}	0.3750	-1.4E-5	0.0
	X _{Si} ^{Ti₅Si₄}	0.4444	4.4E-5	0.0
L + Ti ₅ Si ₄ =TiSi	T(K)	1843	-0.17	0.0
	X _{Si} ^L	0.6044	4.4E-3	0.7
	X _{Si} ^{Ti₅Si₄}	0.4444	4.4E-5	0.0
	X _{Si} ^{TiSi}	0.5000	0	0.0
Ti(β) + Ti ₅ Si ₃ =Ti ₃ Si	T(K)	1435	-7.61	0.5
	X _{Si} ^β	3.61E-2	2.8E-4	0.8
	X _{Si} ^{Ti₅Si₃}	0.3572	-7.8E-3	2.2
	X _{Si} ^{Ti₃Si}	0.25	0	0.0
Ti(β)=Ti(α) + Ti ₃ Si	T(K)	1139	6.38	0.6
	X _{Si} ^β	1.17E-2	6.6E-4	5.3
	X _{Si} ^α	4.88E-3	-1.62E-3	24.9
	X _{Si} ^{Ti₃Si}	0.25	0	0.0

*(experimental – calculated)/experimental.

close to the experimental data [5]. From the nine invariant equilibria of the Ti-Si system, only one of the 32 calculated values presented a considerable relative deviation (over 10%) in relation to the experimental values: the value of the limit of solubility of Ti(α) phase in the eutectoid reaction $Ti(\beta) = Ti(\alpha) + Ti_3Si$, due to the lack of reliable experimental data concerning this equilibrium. Additionally, there is an essential difference of $\sim 6\%$ in the eutectic composition of the liquid ($L = TiSi_2 + Si$) given in Table 4. This difference is probably due to the high tendency of the liquid of the Ti-Si system to local ordering in high concentrations of Si. This same deviation between experimental and calculated values using the regular solution model to describe the liquid phase was observed Seifert et al. [8]. They solved this discrepancy by using a partially ionic liquid model to describe the liquid phase, which is not a common procedure

for metallic systems. If ordering of the liquid is a feasible hypothesis, which seems to be in agreement by the large amount of intermediate phases in the Ti-Si system, the use of other thermodynamic models to describe the liquid phase, such as the associated liquid or quasi-chemical, would result in a better fit between calculated and experimental data, especially in equilibria involving the liquid phase.

The enthalpies of formation of the compounds are presented in Table 5 and these values were compared to previous results [8]. The calculated values for the enthalpies of formation of intermediate phases are nearly equal to those obtained by Seifert et al. [8] and very close to the experimental values shown in Table 2. The calculated Ti-Si phase diagram is shown in Figure 1, showing, additionally, the experimental data used in the present optimization. Figure 2 presents the calculated integral enthalpy of mixing

Table 5. Calculated enthalpies of formation at 298.15K of intermediate phases of Ti-Si system (kJ/mol of atoms)

Ti_5Si_3	Ti_5Si_4	TiSi	$TiSi_2$	Ti_3Si	Reference
-72.67	-79	-77.76	-57.036	-50	Seifert et al. [8]
-72.95	-78.95	-77.53	-58.33	-50	Present work

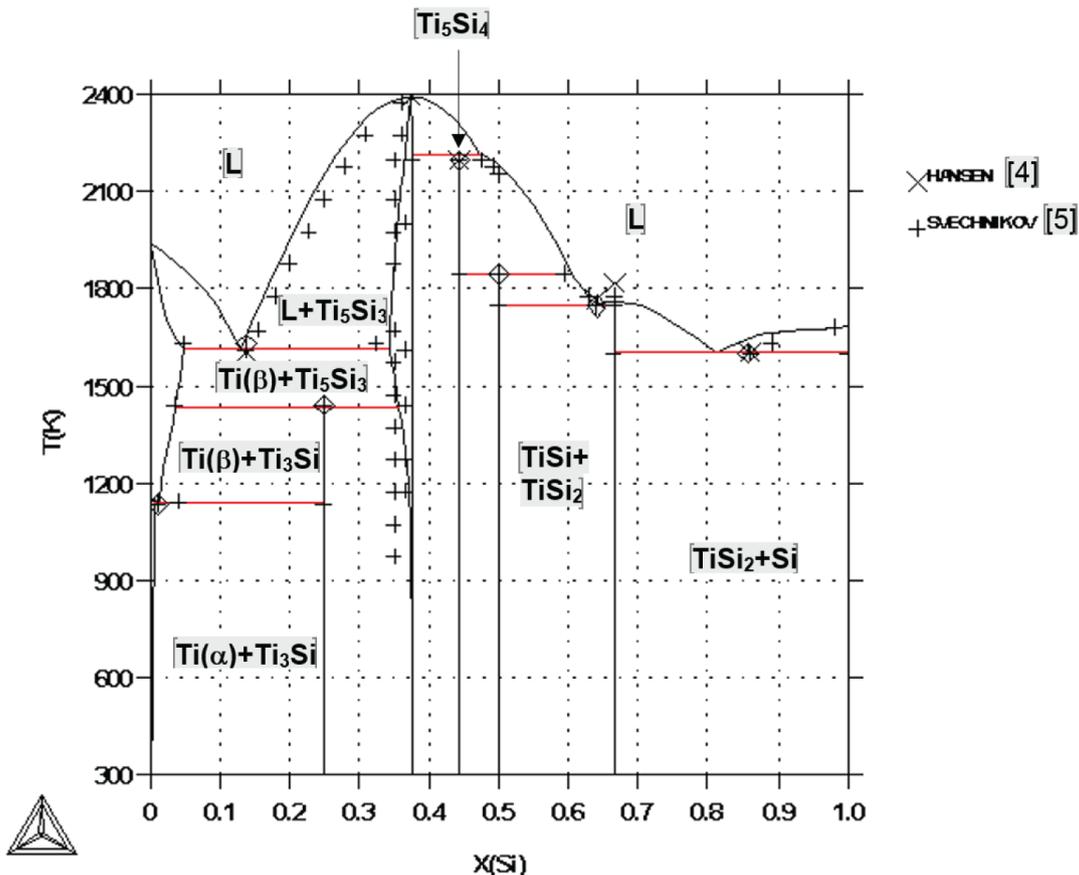


Figure 1. Calculated Ti-Si phase diagram (diamonds correspond to the experimental invariant equilibria listed in Table 1).

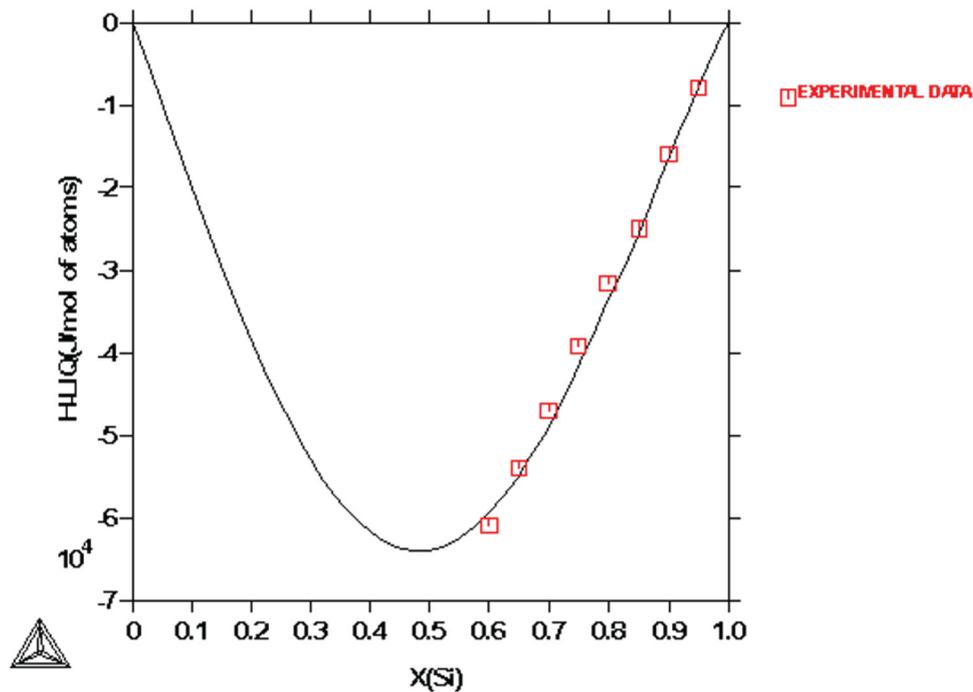


Figure 2. Calculated variation of integral enthalpy of mixture of the liquid of the Ti-Si system at 2000K (J/mol). Experimental data of Esin et al. shown by Vahlas et al. [7].

for the liquid at 2000K along with the experimental data of Esin et al. shown by Vahlas et al. [7]. Both figures indicate that the experimental data are consistent with the calculated values of the present optimization procedure.

The present simplification of the description of the Ti_5Si_3 phase $((Ti)_2(Si,Ti)_3(Ti)_3)$ produced good results when compared to previous assessment [8], allowing its use for the optimization of the Ti-Si-Al phase diagram. This simpler phase description will facilitate the thermodynamic optimization of Ti-Al-Si system, which is the next step of our work.

4 CONCLUSIONS

- The simplification in the description of the Ti_5Si_3 phase $((Ti)_2(Si,Ti)_3(Ti)_3)$ produced a good assessment of the Ti-Si phase diagram, allowing its use for the optimization of the ternary Ti-Si-Al.
- The use of other thermodynamic models to describe the liquid phase, such as the associated liquid or quasi-chemical, might result in a better fit between calculated and experimental data, especially in equilibria involving the liquid phase.

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