Assessment of the Ti-rich corner of the Ti-Si phase diagram using two sublattices to describe the Ti_5Si_3 phase

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Abstract

The thermodynamic optimization of Ti-X-Si systems requires that their respective binary systems be constantly updated. The most recent assessments of the Ti-Si phase diagrams used three sublattices to describe the Ti_5Si_3 phase. The stable version of this phase diagram indicated the presence of $\text{Ti}(\beta) + \text{Ti}_5\text{Si}_3 \rightarrow \text{Ti}_3\text{Si}$ and $\text{Ti}(\beta) \rightarrow \text{Ti}(\alpha) + \text{Ti}_3\text{Si}$ reactions in the Ti-rich corner, while the metastable version featured the presence of a $\text{Ti}(\beta) \rightarrow \text{Ti}(\alpha) + \text{Ti}_5\text{Si}_3$ reaction. The present investigation assessed these phase diagrams using two sublattices to describe the Ti_5Si_3 phase in order to simplify the optimization of Ti-X-Si systems.

Keywords: phase diagram; Ti-Si phase diagram; thermodynamic modeling; Ti_5Si_3 phase; sublattice model.

1. Introduction

There is a technological interest in the Ti-Si system promoted by the beneficial effect of Si addition for the oxidation and creep resistance of Ti-X-Si alloys (Azevedo, 1996). The earliest Ti-Si experimental phase diagram was obtained in 1952 (Hansen *et al.*, 1952), indicating in the Ti-rich corner the presence of a eutectoid reaction at 1133K, $\text{Ti}(\beta) \rightarrow \text{Ti}(\alpha) + \text{Ti}_5\text{Si}_3$. In 1954, another work confirmed the presence of this eutectoid reaction at 1129K (Sutcliffe, 1954). In 1970, a new experimental version of this phase diagram was proposed (Svechnikov *et al.*, 1970), indicating in the Ti-rich corner the presence of two new reactions (a peritectoid reaction at 1444K, $\text{Ti}(\beta) + \text{Ti}_5\text{Si}_3 \rightarrow \text{Ti}_3\text{Si}$ and a eutectoid reaction at 1133K, $\text{Ti}(\beta) \rightarrow \text{Ti}(\alpha) + \text{Ti}_3\text{Si}$), instead of the eutectoid reaction previously observed.

In late 70's, however, careful investigations of the eutectoid reaction of the Ti-Si system were performed without showing any evidence on the presence of the Ti_3Si phase (Plitcha *et al.* 1977; Plitcha and Aaronson, 1978). They confirmed instead the presence of Ti_5Si_3 phase at 1148K, $\text{Ti}(\beta) \rightarrow \text{Ti}(\alpha) + \text{Ti}_5\text{Si}_3$. The first thermodynamic assessment of the Ti-Si phase diagram was performed in 1976 (Kaufmann, 1976) considering the Ti_5Si_3 phase as a stoichiometric intermetallic. Murray (Murray, 1987) assessed the Ti-Si system assuming the Ti_5Si_3 phase as a non-stoichiometric phase and the calculated phase diagram was in agreement with one of the previous results (Svechnikov *et al.*, 1970). In 1996, Seifert *et al.* (Seifert *et al.*, 1996) employed an optimization method for the determination of the variables

used for the thermodynamic description of the phases in order to assess the Ti-Si phase diagram from selected experimental data. They described, for instance, the Ti_5Si_3 phase as a non-stoichiometric compound containing three sublattices, $(\text{Ti})_3(\text{Ti},\text{Si})_2(\text{Si},\text{Ti})_3$, to represent its D_{8h} crystal structure. Their calculated phase diagram was in good agreement with previous calculated (Murray, 1987) and experimental (Svechnikov *et al.*, 1971) phase diagrams, presenting Ti_3Si as the stable phase of the eutectoid reaction. The dispute over the stability of the Ti_3Si phase in Ti-Si and Ti-X-Si systems was, however, far from over. Azevedo (Azevedo, 1996; Azevedo and Flower, 1999; Azevedo and Flower, 2000; Azevedo and Flower, 2002) and Bulanova (Bulanova *et al.*, 1997) identified the

presence of Ti_5Si_3 phase (instead of Ti_3Si) after long isothermal heat treatments below the eutectoid temperature. By contrast, the presence of Ti_3Si phase was observed by other investigations (Kozlov and Pavlyuk, 2004; Ramos *et al.*, 2006; Costa *et al.*, 2010; Li *et al.*, 2014). In 2010, the stability of intermetallic phases in the Ti-Si system

was studied by ab-initio calculations, indicating that the stability of Ti_3Si phase was controversial (Colinet and Tedenac, 2010). Recent ab-initio calculation showed that Ti_5Si_3 phase was actually more stable than Ti_3Si phase at 0 K (Poletaev *et al.*, 2014).

The present work will calculate and compare the Ti-rich corner of the stable

and metastable Ti-Si phase diagrams, using two sublattices, $(Ti,Si)_5(Si,Ti)_3$, to describe the Ti_5Si_3 phase, assuming that Ti_3Si is the stable phase in the eutectoid decomposition of $Ti(\beta)$ phase. These results will be compared to previous calculated phase diagrams using three sublattices to describe the Ti_5Si_3 phase (Cost, 1998; Fiori *et al.*, 2016).

2. Methodology

The liquid, $Ti(\alpha)$ and $Ti(\beta)$ phases are described using Equations 1 to 5. The Gibbs free energy of reference (G^{ref}) is described by Equation 2, while the Gibbs free energy of the ideal solution (G^{id}) is described by Equation 3 and the

excess Gibbs free energy (G^{ex}) of the regular solution is described using the Redlich-Kister polynomial (see Equations 4 and 5) [23]. Additionally, the Gibbs energy for formation of the stoichiometric Ti_3Si phase is described using

the Kopp-Neumann rule (see Equation 6) and the non-stoichiometric Ti_5Si_3 phase is described by the Compound Energy Formalism (Lukas, 2007), using a two-sublattices containing Ti and Si, see Equations 7 to 10.

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

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

Where: $G_i^{ref} = G_i^{SER}$ and x_{Si} and x_{Ti} are the molar fraction of the elements.

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

$$G^{ex} = x_{Si} \cdot x_{Ti} \cdot L_{phase} \quad (4)$$

Where: L_{phase} is the Ti-Si interaction parameter in the phase.

$$L_{phase} = L_{phase}^0 + L_{phase}^1 \cdot (x_{Si} - x_{Ti}) + \dots + L_{phase}^v \cdot (x_{Si} - x_{Ti})^v \quad (5)$$

Where: $L_{phase}^v = a + b \cdot T + \dots$

$$form G^{Ti_3Si} - x_{Ti} \cdot G_{Ti}^{ref} - x_{Si} \cdot G_{Si}^{ref} = a + b \cdot T + c \cdot T \cdot \ln(T) \quad (6)$$

$$G^{Ti_5Si_3} = form G^{Ti_5Si_3} + id G^{Ti_5Si_3} + ex G^{Ti_5Si_3} \quad (7)$$

$$form G^{Ti_5Si_3} = y'_{Ti} \cdot y''_{Ti} \cdot G_{Ti:Ti}^{Ref} + y'_{Si} \cdot y''_{Ti} \cdot G_{Si:Ti}^{Ref} + y'_{Ti} \cdot y''_{Si} \cdot G_{Ti:Si}^{Ref} + y'_{Si} \cdot y''_{Si} \cdot G_{Si:Si}^{Ref} \quad (8)$$

$$id G^{Ti_5Si_3} = R \cdot T \cdot \{ 5 \cdot [y'_{Si} \cdot \ln(y'_{Si}) + y'_{Ti} \cdot \ln(y'_{Ti})] + 3 \cdot [y''_{Si} \cdot \ln(y''_{Si}) + y''_{Ti} \cdot \ln(y''_{Ti})] \} \quad (9)$$

$$ex G^{Ti_5Si_3} = y'_{Ti} \cdot y'_{Si} \cdot (y''_{Ti} \cdot L_{(Ti,Si;Ti)}^{Ti_5Si_3} + y''_{Si} \cdot L_{(Ti,Si;Si)}^{Ti_5Si_3}) + y''_{Ti} \cdot y''_{Si} \cdot (y'_{Ti} \cdot L_{(Ti;Si,Ti)}^{Ti_5Si_3} + y'_{Si} \cdot L_{(Si;Si,Ti)}^{Ti_5Si_3}) + y'_{Ti} \cdot y'_{Si} \cdot y''_{Ti} \cdot y''_{Si} \cdot L_{(Ti,Si;Si,Ti)}^{Ti_5Si_3} \quad (10)$$

Where: y_j^n is the site fraction of the element (j) in the sublattice (n).

The parameters and variables used for the thermodynamic description of the Ti_5Si_3 and Ti_3Si phases are listed in Table 1. These variables were calculated from selected experimental data (see Tables 2 and 3) using the Parrot module of the Thermo-Calc software. The variables

related to the Ti_5Si_3 phase were initially calculated during the assessment of the metastable phase diagram (suspending the presence of the Ti_3Si phase). These variables were then fixed during the assessment of the stable phase diagram for the calculation of the variables related

to the Ti_3Si phase. These diagrams were compared to the stable and metastable Ti-Si phase diagrams obtained by Thermo-calc software using COST 507 database (Cost, 1998), whose Ti-Si system was based on the assessed version by Seifert *et al.* (Seifert *et al.*, 1996).

Table 1
Parameters and variables
used for the thermodynamic
description of the Ti_5Si_3 - $(\text{Ti},\text{Si})_5$:
 $(\text{Si},\text{Ti})_3$ - and Ti_3Si phases. V_{i1} in $[\text{J} \cdot (\text{mol of phase})^{-1}]$; V_{i2} in $[\text{J} \cdot (\text{mol of phase})^{-1} \cdot \text{K}^{-1}]$.

Thermodynamic function	Parameters	Variables
Gibbs energy for the formation of Ti_5Si_3	${}^0G_{\text{Ti}_5\text{Si}_3}^{\text{hcp}} - [5 \cdot G_{\text{Ti}}^{\text{hcp}}(\text{T}) + 3 \cdot G_{\text{Si}}^{\text{diamond}}(\text{T})]$	$V11 + V12 \cdot \text{T}$
Gibbs energy for the formation of hypothetical Ti_8	${}^0G_{\text{Ti}_8\text{Ti}}^{\text{hcp}} - [8 \cdot G_{\text{Ti}}^{\text{hcp}}(\text{T})]$	$(40,000 + 20 \cdot \text{T})^*$
Gibbs energy for the formation of hypothetical Si_8	${}^0G_{\text{Si}_8\text{Si}}^{\text{diamond}} - [8 \cdot G_{\text{Si}}^{\text{diamond}}(\text{T})]$	$V21 + V22 \cdot \text{T}$
Gibbs energy for the formation of hypothetical Ti_3Si_5	${}^0G_{\text{Ti}_3\text{Si}_5}^{\text{hcp}} - [3 \cdot G_{\text{Ti}}^{\text{hcp}}(\text{T}) + 5 \cdot G_{\text{Si}}^{\text{diamond}}(\text{T})]$	$V31 + V32 \cdot \text{T}$
Excess Gibbs energy for the $(\text{Si},\text{Ti}:\text{Ti})$ interaction	${}^0L_{\text{Si,Ti,Ti}}^{\text{Ti}_5\text{Si}_3}$	$V41 + V42 \cdot \text{T}^{**}$
Excess Gibbs energy for the $(\text{Si},\text{Ti}:\text{Si})$ interaction	${}^0L_{\text{Si,Ti,Si}}^{\text{Ti}_5\text{Si}_3}$	$V41 + V42 \cdot \text{T}^{**}$
Excess Gibbs energy for the $(\text{Ti}:\text{Si},\text{Ti})$ interaction	${}^0L_{\text{Ti,Si,Ti}}^{\text{Ti}_5\text{Si}_3}$	$V51 + V52 \cdot \text{T}^{**}$
Excess Gibbs energy for the $(\text{Si}:\text{Si},\text{Ti})$ interaction	${}^0L_{\text{Si,Si,Ti}}^{\text{Ti}_5\text{Si}_3}$	$V51 + V52 \cdot \text{T}^{**}$
Excess Gibbs energy for the $(\text{Si},\text{Ti}:\text{Si},\text{Ti})$ interaction	${}^0L_{\text{Si,Ti,Si,Ti}}^{\text{Ti}_5\text{Si}_3}$	$V61 + V62 \cdot \text{T}^{**}$
Gibbs energy for the formation of Ti_3Si phase	${}^0G_{\text{Ti}_3\text{Si}}^{\text{hcp}} - [3 \cdot G_{\text{Ti}}^{\text{hcp}}(\text{T}) + G_{\text{Si}}^{\text{diamond}}(\text{T})]$	$V71 + V72 \cdot \text{T}$

* (Cost, 1998); ** ${}^0L_{\text{Si,Ti,Ti}}^{\text{Ti}_5\text{Si}_3} = {}^0L_{\text{Si,Ti,Si}}^{\text{Ti}_5\text{Si}_3}$ and ${}^0L_{\text{Ti,Si,Ti}}^{\text{Ti}_5\text{Si}_3} = {}^0L_{\text{Si,Si,Ti}}^{\text{Ti}_5\text{Si}_3}$ (Lukas, 2007).

Ti_3Si	Ti_5Si_3	Ti_5Si_4	TiSi	TiSi_2	Type	Reference
-50.0	-72.67	-79.0	-77.76	-57.036	Optimization	(Svechnikov et al. 1970)
-47.11	-72.53	-74.63	-72.23	-49.87	Ab-initio	(Colinet and Tedenac, 2014)
-	-72.52	-	-	-56.97	Experimental	(Robins and Jenkins, 1955; Topor and Kleppa, 1996; Maslov et al., 1978)
-	-78.1	-75.9	-71.5	-53.5	Experimental	(Kematack and Myers, 1996)
-49	-73.8	-78.5	-72.6	-55	Experimental	(Meschel and Kleppa, 1998; Coelho et al., 2006)

Table 2
Enthalpy for the formation of intermetallic
phases, Ti-Si system (kJ/mol of phase).

3. Results and discussion

The calculated values of the variables are shown in Table 4. According to Thermo-Calc User Guide (Thermo, 2015), the order of magnitude of V_{i1} -type variables should not be higher than 10^5 and the V_{i2} -type variables should not be higher than 10^1 . In the present

assessments $V11$ presented an order of magnitude above 10^5 ; and $V52$ above 10^1 . This V_{i2} -type variable, however, was used to describe the excess term of the enthalpy rather than the entropy for the formation of intermetallic phases. The values of the reduced sum of squares

(~ 5 for both optimization procedures) exceeded the advisable maximum value of one (Thermo, 2015). These results indicate that the optimization procedures of the Ti-Si system using two sublattices to describe the Ti_5Si_3 phase were successful but they can be further improved.

Table 3
Experimental values of the Ti-Si invariant
reactions ($X_{\text{Si}}^{\text{phase}}$: atomic fraction of Si).

Reaction	T(K)	Experimental values			References
$\text{L} \rightarrow \text{Ti}_5\text{Si}_3$	2401	$X_{\text{Si}}^{\text{L}} = 0.375$	$X_{\text{Si}}^{\text{Ti}_5\text{Si}_3} = 0.375$	-	(Hansen et al., 1952; Sutcliffe, 1954; Svechnikov et al. 1970; Plitcha et al. 1977; Plitcha and Aaronson, 1978; Seifert et al. 1996)
$\text{L} \rightarrow \text{TiSi}_2$	1773	$X_{\text{Si}}^{\text{L}} = 0.667$	$X_{\text{Si}}^{\text{TiSi}_2} = 0.667$	-	
$\text{L} \rightarrow \beta + \text{Ti}_5\text{Si}_3$	1613	$X_{\text{Si}}^{\text{L}} = 0.137$	$X_{\text{Si}}^{\beta} = 0.047$	$X_{\text{Si}}^{\text{Ti}_5\text{Si}_3} = 0.36$	
$\text{L} \rightarrow \text{TiSi}_2 + \text{Si}$	1603	$X_{\text{Si}}^{\text{L}} = 0.86$	$X_{\text{Si}}^{\text{TiSi}_2} = 0.667$	$X_{\text{Si}}^{\text{Si}} = 1$	
$\text{L} \rightarrow \text{TiSi}_2 + \text{TiSi}$	1747	$X_{\text{Si}}^{\text{L}} = 0.641$	$X_{\text{Si}}^{\text{TiSi}} = 0.5$	$X_{\text{Si}}^{\text{TiSi}_2} = 0.667$	
$\text{L} + \text{Ti}_5\text{Si}_3 \rightarrow \text{Ti}_5\text{Si}_4$	2193	$X_{\text{Si}}^{\text{L}} = 0.48$	$X_{\text{Si}}^{\text{Ti}_5\text{Si}_3} = 0.398$	$X_{\text{Si}}^{\text{Ti}_5\text{Si}_4} = 0.444$	
$\text{L} + \text{Ti}_5\text{Si}_4 \rightarrow \text{TiSi}$	1843	$X_{\text{Si}}^{\text{L}} = 0.60$	$X_{\text{Si}}^{\text{Ti}_5\text{Si}_4} = 0.444$	$X_{\text{Si}}^{\text{TiSi}} = 0.5$	
$\beta + \text{Ti}_5\text{Si}_3 \rightarrow \text{Ti}_3\text{Si}$	1443	$X_{\text{Si}}^{\beta} = 0.04$	$X_{\text{Si}}^{\text{Ti}_5\text{Si}_3} = 0.36$	$X_{\text{Si}}^{\text{Ti}_3\text{Si}} = 0.25$	
$\beta \rightarrow \alpha + \text{Ti}_3\text{Si}$	1149	$X_{\text{Si}}^{\beta} = 0.009$	$X_{\text{Si}}^{\alpha} = 0.004$	$X_{\text{Si}}^{\text{Ti}_3\text{Si}} = 0.25$	
$\beta \rightarrow \alpha + \text{Ti}_5\text{Si}_3$ (metastable)	1133	$X_{\text{Si}}^{\beta} = 0.011$	$X_{\text{Si}}^{\alpha} = 0.005$	$X_{\text{Si}}^{\text{Ti}_5\text{Si}_3} = 0.365$	

Description	Variables	Calculated values
Gibbs energy for the formation of Ti_5Si_3	V11	-592,126.51
	V12	6.055
Gibbs energy for the formation of hypothetical Si_8	V21	-36,405.66
	V22	12.595
Gibbs energy for the formation of hypothetical Ti_3Si_5	V31	-15,172.13
	V32	5.055
Excess terms, (Si,Ti:Ti) and (Si,Ti:Ti) interactions, Ti_5Si_3	V41	49,843.69
	V42	-16.271
Excess terms, (Si:Si,Ti) and (Ti:Si,Ti) interactions, Ti_5Si_3	V51	-624.781
	V52	335.78
Excess term, (Si,Ti:Si,Ti) interaction, Ti_5Si_3	V61	-226.340
	V62	-14.165
Gibbs energy for the formation of Ti_3Si	V71	-200,788.05
	V72	2.737

Table 4
Calculated variables, V_{i1} in [J.(mol of phase)⁻¹]; V_{i2} in [J.(mol of phase)⁻¹.K⁻¹].

Reaction	Parameter	Experimental	Calculated	Deviation (%)
$L \rightarrow Ti_5Si_3$	T (K)	2403	2394	0.4
	$X_{Si}^{Ti_5Si_3}$	0.375	0.375	0
$L \rightarrow TiSi_2$	T (K)	1773	1757	1
	$X_{Si}^{TiSi_2}$	0.667	0.667	0
$L \rightarrow \beta + Ti_5Si_3$	T (K)	1613	1626	0.6
	X_{Si}^L	0.137	0.127	7
	X_{Si}^β	0.047	0.044	4
	$X_{Si}^{Ti_5Si_3}$	0.36	0.35	5
$L \rightarrow TiSi_2 + Si$	T (K)	1603	1604	0.1
	X_{Si}^L	0.86	0.815	5
	$X_{Si}^{TiSi_2}$	0.667	0.667	0
	X_{Si}^{Si}	1	1	0
$L \rightarrow TiSi_2 + TiSi$	T (K)	1747	1747	0
	X_{Si}^L	0.641	0.637	0.7
	X_{Si}^{TiSi}	0.5	0.50	0
	$X_{Si}^{TiSi_2}$	0.667	0.667	0
$L + Ti_5Si_3 \rightarrow Ti_5Si_4$	T (K)	2193	2210	0.8
	X_{Si}^L	0.477	0.476	0.2
	$X_{Si}^{Ti_5Si_3}$	0.405	0.375	6
	$X_{Si}^{Ti_5Si_4}$	0.444	0.444	0
$L + Ti_5Si_4 \rightarrow TiSi$	T (K)	1843	1843	0
	X_{Si}^L	0.60	0.604	0.7
	$X_{Si}^{Ti_5Si_4}$	0.444	0.444	0
	X_{Si}^{TiSi}	0.5	0.5	0
$\beta + Ti_5Si_3 \rightarrow Ti_3Si$	T (K)	1443	1457	0.1
	X_{Si}^β	0.04	0.033	18
	$X_{Si}^{Ti_5Si_3}$	0.36	0.353	2
	$X_{Si}^{Ti_3Si}$	0.25	0.25	0
$\beta \rightarrow \alpha + Ti_3Si$	T (K)	1149	1142	0.8
	X_{Si}^β	0.009	0.010	6
	X_{Si}^α	0.004	0.0042	5
	$X_{Si}^{Ti_3Si}$	0.25	0.25	0
	$H_{form}^{Ti_3Si}$ (J/mol of phase)	-47,850	-50,197	5
$\beta \rightarrow \alpha + Ti_5Si_3$ (metastable)	T (K)	1133	1138	0.4
	X_{Si}^β	0.011	0.013	18
	X_{Si}^α	0.005	0.0054	8
	$X_{Si}^{Ti_5Si_3}$	0.365	0.36	1.4
	$H_{form}^{Ti_5Si_3}$ (J/mol of phase)	-73,874	-74,016	0.2

Table 5
Main experimental and calculated values of the Ti-Si system.

Table 5 compares the values of the experimental and the calculated equilibria and the enthalpies for the formation of Ti_3Si and Ti_5Si_3 phases. Six out of the 38 calculated values presented relative deviation above 5% in relation to the experimental data. Two of these deviations were origi-

nated in the equilibria involving the liquid phase and they could be decreased by the use of a more complex model for the thermodynamic description of the liquid phase (Lukas, 2007; Seifert *et al.*, 1996; Fiori *et al.*, 2016). The other values were found for the $\beta + Ti_5Si_3 \rightarrow Ti_3Si$, $\beta \rightarrow \alpha + Ti_3Si$ and $\beta \rightarrow \alpha + Ti_5Si_3$

reactions, indicating that further experiments in these critical regions of the Ti-rich corner of the Ti-Si phase diagram are needed to improve the results of the present optimization procedures; and to define which one of the eutectoid reactions is actually the stable one ($\beta \rightarrow \alpha + Ti_3Si$ or $\beta \rightarrow \alpha + Ti_5Si_3$).

Figure 1
Stable Ti-Si phase diagram. a) General view of the phase diagram ($\beta + Ti_5Si_3 \rightarrow Ti_3Si$ and $\beta \rightarrow \alpha + Ti_3Si$ reactions) compared with the latest assessment (Fiore *et al.*, 2016); b) Detail of the eutectoid reaction, $Ti(\beta) \rightarrow Ti(\alpha) + Ti_3Si$ in the Ti-rich corner, compared with previous assessment by COST 507 database (Cost, 1998).

Figure 2
Metastable Ti-Si phase diagram. a) General view of the Ti-Si phase diagram ($\beta \rightarrow \alpha + Ti_5Si_3$ reaction) compared with the latest assessment (Fiore *et al.*, 2016); b) Detail of the eutectoid reaction, $Ti(\beta) \rightarrow Ti(\alpha) + Ti_5Si_3$, in the Ti-rich corner, compared with previous assessment by COST 507 database (Cost, 1998) with suspended Ti_3Si phase.

Figure 1-a shows a general view of the calculated stable Ti-Si phase diagram, indicating that the position of the phase boundaries are in fair agreement with previous results (Svehnikov *et al.* 1970; Fiore *et al.* 2016), except for the narrower solubility range of the Ti_5Si_3 phase field. Figure 1-b shows a detail of the Ti-rich corner near the eutectoid reaction, indicating that there are no experimental data to validate the position of the calculated $Ti(\alpha)$ and $Ti(\beta)$ solvus lines. The present assessment showed lower Si-solubility in the $Ti(\alpha)$ and $Ti(\beta)$ phases when compared to the calculated phase diagram using COST 507 database (Cost, 1998), without any change in the eutectoid temperature.

Figure 2-a shows the calculated metastable Ti-Si phase diagram, indicating that the position of the phase boundaries are in good agreement with previous experimental (Hansen *et al.*, 1952; Sutcliffe, 1954) and calculated (Fiore *et al.* 2016) phase diagrams, except for the narrower sol-

ubility range of the Ti_5Si_3 phase field. The shape of this phase field resembles a previous result, which described the Ti_5Si_3 phase as $Ti_3Ti_2(Ti,Si)_3$ (Beneduce *et al.*, 2016). Figure 2-b shows a detail of the Ti-rich corner near the eutectoid reaction, comparing the present assessment with previous experimental (Plitcha *et al.* 1977; Plitcha and Aaronson, 1978) and calculated (Cost, 1998; Fiore *et al.* 2016) phase diagrams. The present assessment showed smaller Si-solubility in the $Ti(\alpha)$ and $Ti(\beta)$ phases when compared to the calculated phase diagram using COST 507 database (Cost, 1998) and a slightly higher value for the eutectoid temperature. The slope of the $Ti(\alpha)$ solvus line showed a typical inclination, unlike the one obtained by COST 507 database (Cost, 1998), indicating that the Si solubility of the $Ti(\alpha)$ phase decreased with decreasing temperature. This result is agreement with the most recent assessment of the metastable Ti-Si phase diagram (Fiore *et al.* 2016).

The position of the Ti_5Si_3 phase field in both assessments was slightly shifted towards smaller Si contents. Additionally, its Si-solubility range was comparatively narrower and presented a maximum of 37.5at%. This maximum Si-solubility value suggests that the present thermodynamic description of the excess terms of the $(Ti,Si)_5(Si,Ti)_3$ phase was not able to induce the presence of Si atoms on the Ti sublattice. In this sense, the hypothesis that the interaction between Si and Ti on each sublattice is independent of the occupation of the other sublattice (${}^0L_{Si,Ti;Ti}^{Ti_5Si_3} = {}^0L_{Si,Ti;Si}^{Ti_5Si_3}$ and ${}^0L_{Ti,Ti;Ti}^{Ti_5Si_3} = {}^0L_{Ti,Ti;Si}^{Ti_5Si_3}$), see

Table 1) should be further analyzed. For instance, another hypothesis, assuming that the interaction parameters on the two sublattices are symmetrical (${}^0L_{Si,Ti;Ti}^{Ti_5Si_3} = {}^0L_{Ti,Ti;Si}^{Ti_5Si_3}$ and ${}^0L_{Si,Ti;Si}^{Ti_5Si_3} = {}^0L_{Ti,Ti;Ti}^{Ti_5Si_3}$), can

be investigated. Finally, the description of the Ti_5Si_3 phase using only two sublattices presented promising results for the assessment of Ti-X-Si phase diagrams.

4. Conclusions

- The assessed versions of the stable and metastable Ti-Si phase diagrams, using only two sublattices to describe the Ti_5Si_3 phase, were in fair agreement with previous experimental and calculated phase diagrams.

- The slope of the $Ti(\alpha)$ solvus line of the assessed metastable Ti-Si phase diagram showed a typical inclination, indicating that the Si-solubility of the $Ti(\alpha)$ phase decreased with decreasing temperature.

- The position of the Ti_5Si_3 phase field in both assessments was slightly shifted towards smaller Si contents. Additionally, its Si-solubility range was comparatively much narrower than expected and presented a maximum value of 37.5at%.

- The assessment of the Ti-Si phase diagram using two sublattices to describe the Ti_5Si_3 phase might be further improved by the inclusion of new experimental data near the eutectoid

reaction of the Ti-rich corner of the Ti-Si phase diagram. In this sense, further experimental work is needed to define which eutectoid reaction ($\beta \rightarrow \alpha + Ti_5Si_3$ or $\beta \rightarrow \alpha + Ti_3Si$) is stable.

- Finally, the use of a more complex description for the liquid phase and another thermodynamic description for the excess terms of the Ti_5Si_3 phase might be useful to improve the quality of the assessed phase diagrams.

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References

- AZEVEDO, C. R. F. Phase diagram and phase transformations in Ti-Al-Si System. Imperial College, Department of Materials, 1996. (PhD Thesis).
- AZEVEDO, C. R. F., FLOWER, H. M. Microstructure and phase relationships in Ti-Al-Si system. *Materials Science and Technology*, v. 15, n.8, p.869-877, 1999.
- AZEVEDO, C. R. F., FLOWER, H. M. Calculated ternary diagram of Ti-Al-Si system. *Materials Science and Technology*, v. 16, p.372-381, 2000.
- AZEVEDO, C. R. F., FLOWER, H. M. Experimental and calculated Ti-rich Corner of the Ti-Al-Si Ternary Phase Diagram. *Calphad*, v.26, p.353-373, 2002.
- BENEDUCE NETO, F., FIORE, M., AZEVEDO, C. R. F. Simplification of the thermodynamic description of the Ti-Si system. *Tecnol. Metal. Mater. Miner.*, v. 13, p. 91-97, 2016.
- BULANOVA, M., TRETYACHANKO, L., AND GOLOVKOVA, M. Phase equilibria in the Ti-rich corner of the Ti-Al-Si System. *Z. Metallkd.* v. 88, n. 3, p.256-265, 1997.
- COELHO, G. C., DAVID, N., GACHON, J. C., NUNES, C. A., FIORANI, J. M., VILASI, M. Entalpias de formação de fases intermetálicas dos sistemas Ti-Si, Ti-B e Ti-Si-B medidas por calorimetria de síntese direta. In: CONGRESSO DA ABM, 61, Rio de Janeiro. Anais... São Paulo, Associação Brasileira de Metalurgia e Materiais, 2006. p. 1300-1308.
- COLINET, C., TEDENAC, J. C. Structural stability of intermetallic phases in the Si-Ti system. Point defects and chemical potentials in $D8_8-Si_3Ti_5$ phase. *Intermetallics*, v. 18, p.1444-1454, 2010.
- COST 507. Definition of Thermochemical and Thermophysical Properties to Provide a Database for the Development of New Light Alloys. European Cooperation in the Field of Scientific and Technical Research, European Commission. Proceedings of the Final Workshop of COST 507, Vaals, the Netherlands, 1998.
- COSTA, A. M. S., LIMA, G. F., NUNES, C. A., COELHO, G. C., AND SUZUKI, P. A. Evaluation of Ti_5Si_3 phase stability from heat-treated rapidly solidified Ti-Si alloys. *Journal of Phase Equilibria and Diffusion*, v.31, p.22-27, 2010.
- FIORE, M., BENEDUCE NETO, F., AND AZEVEDO, C. R. F. Assessment of the Ti-rich corner of the Ti-Si phase diagram: the recent dispute about the eutectoid reaction. *Materials Research*, v.19, p.942-953, 2016.
- HANSEN, M., KESSLER, H. D., MCPHERSON, D. J. Ti-Si phase diagram. *Transactions ASM*, v.44, p.518-538, 1952.
- KAUFFMAN, L. Coupled phase diagrams and thermochemical data for transition metal binary systems-VI*, *Calphad*, v. 3, n.1, p.45-76, 1979.
- KEMATICK, R. J., MYERS, C. E. Thermodynamics of the Phase Formation of the Titanium Silicides. *Chemistry of Materials*, v. 8, n. 1, p.287-291, 1996.

- KOZLOV, A. K., PAVLYUK, V. V. Investigation of the interaction between the components in the Ti-(Si, Ge)-Sb systems at 670 K. *Journal of Alloys and Compounds*, v. 367, p.76-79, 2004.
- LI, Z., LIU, Y., WANG, X., WU, Y., ZHAO, M., LONG, Z., YIN, F. 700°C isothermal section of the Al-Ti-Si ternary phase diagram. *Journal of Phase Equilibria and Diffusion*, v.35, p.564-574, 2014.
- LUKAS, H. L., FRIES, S. G., SUNDMAN, B. *Computational thermodynamics: the calphad method*. Cambridge University Press, 2007.
- MASLOV, V.M., NEGANOV, A.S., BOROVINSKAYA, I.P., AND MERZHANOV, A.G. Self-propagating high-temperature synthesis as a method for determination of the heat of formation of refractory compounds. *Combust. Explos. Shock Waves*, v. 14, n. 6, p.759-767, 1978.
- MESCHEL, S., KLEPPA, O. Standard enthalpies of formation of some 3d transition metal silicides by high temperature direct synthesis calorimetry. *Journal of Alloys and Compounds*, v. 267, n. 1-2, p.128-135, 1998.
- MURRAY, J. L. *Phase diagrams of titanium binary alloys*. Ohio: ASM International, 1987. p. 289-293.
- PLICHTA M. R., WILLIAMS, J. C., AARONSON, H. I. On the existence of the $\beta \rightarrow \alpha_m$ transformation in the alloy systems Ti-Ag, Ti-Au, and Ti-Si. *Metallurgical Transactions A*, v. 8, p.1885-1892, 1977.
- PLITCHA, M. R., AARONSON, H. I. The thermodynamic and kinetics of the $\beta \rightarrow \alpha_m$ transformation in three Ti-X systems. *Acta Metallurgica*, v. 26, p.1293-1305, 1978.
- POLETAEV, D. O., LIPNITSKII, A. G., KARTAMYSHEV, A. I., AKSYONOV, D.A., TKACHEV, E.S., MANOKHIN, S. S., IVANOV, M. B., KOLOBOV, Y. R. Ab initio-based prediction and TEM study of silicide precipitation in titanium. *Computational Materials Science*, v. 95, p.456-463, 2014.
- RAMOS, A. S., NUNES, C. A., COELHO, G. C. On the peritectoid Ti_3Si formation in Ti-Si alloys. *Materials Characterization*, v. 56, p.107-11, 2006.
- ROBINS, D. A., JENSKINS, I. The heats of formation of some transition metal silicides. *Acta Metallurgica*. v.3, p.598-603, 1955.
- SEIFERT, H. J., LUKAS, H. L., PETZOW, G. Thermodynamic optimization of the Ti-Si system. *Z. Metallkd*, v. 87, p.2-13, 1996.
- SUTCLIFFE, D. A. Alliage de titane et de silicium. *Revue de Metallurgie*, n.3, p.524-536, 1954.
- SVECHNIKOV V. N., KOCHERZHISKY Y. A., YUPKO L. M., KULIK, O.G., SHINSHKIN, E. A. Phase diagram of the titanium-silicon system. *Dokl. Akad. SSSR*, v. 193, n. 2, p.393-396, 1970.
- Thermo-Calc. Data optimization User Guide, Version 2015a. Foundation of Computational Thermodynamics Stockholm, Sweden. Last assessed in November 15th, 2015. <http://www.thermocalc.com/media/30890/Data-Optimisation-User-Guide-for-Thermo-Calc.pdf>
- TOPOR, L., KLEPPA, O. J. Standard enthalpies of formation of TiSi_2 and VS_2 by high-temperature calorimetry. *Metallurgical Transactions A*, v.17, p.1217-1221, 1986.

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