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Thermodynamic description of the Cr–Sn–Ti system

Yongliang Gao, Cuiping Guo, Changrong Li, Zhenmin Du*

Department of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

The Cr–Sn–Ti system was optimized by the means of the CALPHAD (CALculation of PHAse Diagram) technique. The solution phases (liquid, hcp, bcc and bct) were described by the substitutional-solution model. The compounds Sn_3Ti_2, Sn_5Ti_6 and Sn_3Ti_5 were treated as $(Sn)_m(Cr, Ti)_n$ by a two-sublattice model in the Cr–Sn–Ti system. The compounds $SnTi_2$ and $SnTi_3$ were treated as $(Sn, Va)_1(Cr, Ti, Va)_2$ and $(Sn, Va)_1(Cr, Ti)_3$ by a two-sublattice model in the Cr–Sn–Ti system, respectively. The Laves phases αCr_2Ti, βCr_2Ti and γCr_2Ti were described as $(Cr, Sn, Ti)_2(Cr, Sn, Ti)_1$ in the Cr–Sn–Ti system. A self-consistent thermodynamic description of the Cr–Sn–Ti system was obtained.

1. Introduction

Chromium by itself possesses a very unusual anti-ferromagnetism and this property is drastically modified by addition of other elements, for example Sn, which increases Cr Neel temperature. Consequently Chromium–Tin alloys are used for precision materials [1]. Recently, more and more attentions have been paid for expanding the markets of titanium alloys in aerospace and automotive industry, owing to both the demand of growth of titanium alloys industry and the decrease of energy consumption of vehicles [2,3]. It is very important to optimize alloy compositions with the knowledge of phase equilibria. The combination of experiments and thermodynamic calculations is a powerful strategy when investigating phase equilibria in multi-component systems.

This work deals with a thermodynamic assessment of the Cr–Sn–Ti system by means of the CALPHAD (CALculation of PHAse Diagram) technique. In this method, the thermodynamic properties of the ternary alloy systems are studied using thermodynamic models for the Gibbs energy of the individual phases. The thermodynamic parameters involved in the models are optimized according to the experimental thermodynamic and phase diagram information in the literature.

2. Binary sub-systems

To obtain a thermodynamic description of a ternary system, the thermodynamic description of each involved binary sub-system is necessary.

2.1. Cr–Sn sub-system

The Cr–Sn sub-system was first assessed by Venkatraman and Neumann [4], while no thermodynamic parameters were given. The thermodynamic description of the Cr–Sn sub-system was re-optimized by Jerlerud Pérez and Sundman [1] and used in the present work. Fig. 1 is the Cr–Sn phase diagram calculated using the thermodynamic parameters of Jerlerud Pérez and Sundman [1].

2.2. Cr–Ti sub-system

The Cr–Ti sub-system has been assessed by Molokanov et al. [5], Kaufman and Nesor [6], Murray [7,8], Saunders [9], Lee et al. [10], Zhuang [11] and Ghosh [12]. Molokanov et al. [5] did not consider the Laves phase Cr_2Ti. In the works of Kaufman and Nesor [6] and Murray [7,8], the αCr_2Ti phase was treated as a stoichiometric compound, and its polymorphic transformations were neglected. Like many other Cr-based Laves phases, Cr_2Ti exhibits polytypism in the forms of C15 (αCr_2Ti), C36 (βCr_2Ti) and C14 (γCr_2Ti) structures [12]. Because Cr_2Ti Laves phases are always nonstoichiometric and Cr atoms occupy two different lattice sites [13], αCr_2Ti, βCr_2Ti and γCr_2Ti were treated as $(Cr, Ti)_2(Cr, Ti)$ by Ghosh [12] assuming antistructure atoms on both sublattics. In general, the assessed results of Ghosh [12] comparing with the previous work [9–11] show a good agreement with the experimental results [11,13–16].

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* Corresponding author. Tel.: +86 10 6233 3772; fax: +86 10 6233 3772.
E-mail address: zmdu2@hotmail.com (Z. Du).

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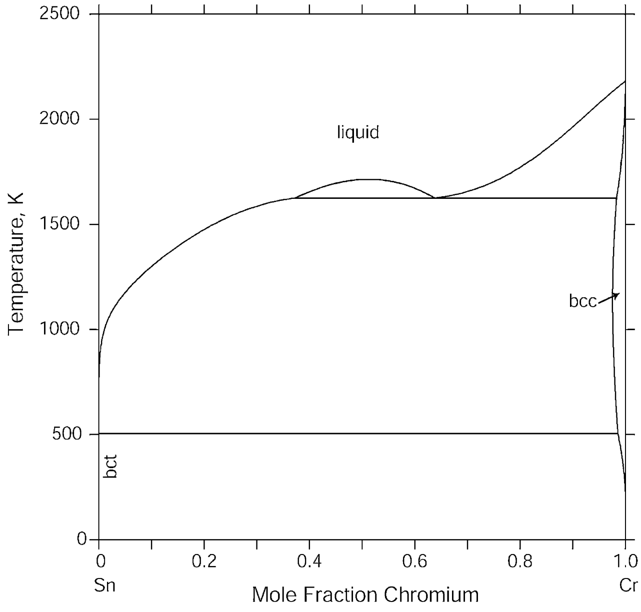

Fig. 1. Calculated Cr–Sn phase diagram using the thermodynamic description of Jerlerud Perez and Sundman [1].

The thermodynamic parameters of the Cr–Ti sub-system optimized by Ghosh [12] are adopted in this work. Fig. 2 shows the Cr–Ti phase diagram calculated using the thermodynamic description of Ghosh [12].

2.3. *Sn–Ti sub-system*

There are four solution phases liquid, bcc, bct and hcp, and five intermetallic compounds Sn_3Ti_2, Sn_5Ti_6, Sn_3Ti_5, $SnTi_2$ and $SnTi_3$ in the Sn–Ti sub-system. The Sn–Ti sub-system was assessed by Kaufman and Nesor [17], Murray [18], Hayes [19], Liu et al. [20] and Yin et al. [21]. In earlier work [17,18], the $SnTi_2$ and $SnTi_3$ phases were treated as stoichiometric compounds. In the works of Hayes [19] and Liu et al. [20], $SnTi_3$ was treated by a two-sublattice model (Sn, Ti)(Sn, $Ti)_3$ and other compounds were treated as stoichiometric phases. Most recently, Yin et al. [21] reassessed the Sn–Ti sub-system based on their experimental results in Sn-rich portion. In the work of Yin et al. [21], the compound $SnTi_2$ with $InNi_2$-type structure ($B8_2$) was treated using a two-sublattice model (Sn, Va)(Ti, $Va)_2$ to describe the homogeneity range of 32.7–35.9 at.% Sn, where Va means vacancy; and $SnTi_3$ was treated as (Sn, Va)$(Ti)_3$ because of its homogeneity range (23–25 at.% Sn) extending only towards the rich-Ti side, and considering the big difference of the atom radii between Ti and Sn atoms. The thermodynamic description of the Sn–Ti sub-system obtained by Yin et al. [21] is adopted in the present work. Fig. 3 shows the calculated Sn–Ti phase diagram using the thermodynamic parameters of Yin et al. [21].

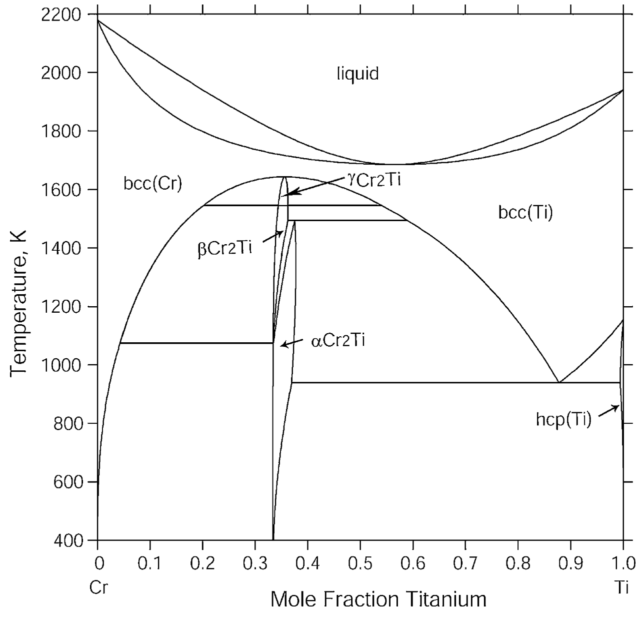

Fig. 2. Calculated Cr–Ti phase diagram using the thermodynamic description of Ghosh [12].

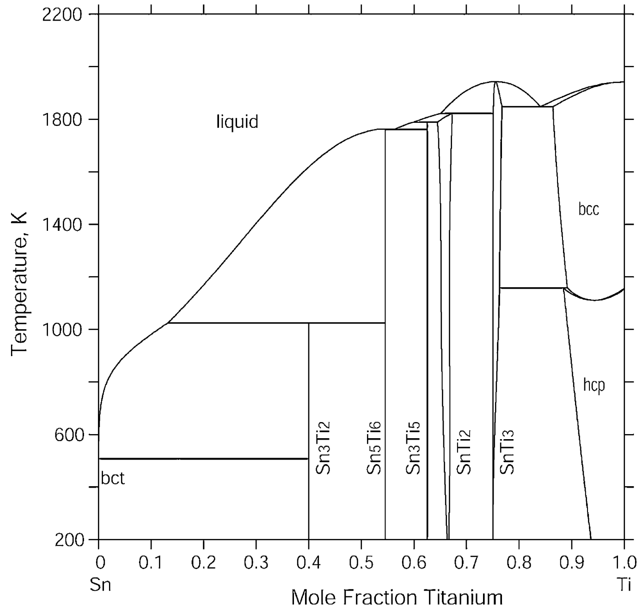

Fig. 3. Calculated Sn–Ti phase diagram using the thermodynamic description of Yin et al. [21].

3. Experimental information on the Cr–Sn–Ti system

The information about the Cr–Sn–Ti system is very scarce. Recently, Aricó and Gribaudo [22] presented the isothermal section at 1173 K and 1373 k based on the experimental and estimated results. Two and three phase equilibria and several experimental tie lines of conjugated phases in quilibria were given for the whole range of compositions of the ternary system. No ternary compounds were found. There was a considerable solubility of chromium in the Sn_3Ti_5, $SnTi_2$ and $SnTi_3$ compounds.

4. Thermodynamic models

4.1. *Unary phases*

The Gibbs energy function $G_i^{\phi}(T) = {}^0G_i^{\phi}(T) - H_i^{\mathrm{SER}}$ (298.15 K) for the element i (i = Cr, Sn, Ti) in the phase ϕ (ϕ = liquid, bcc, hcp or bct) is described by an equation of the following form,

$$G_i^{\phi}(T) = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \tag{1}$$

where H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, being bcc for Cr, bct for Sn, and hcp for Ti, respectively. The Gibbs energy of the element i, $G_i^{\phi}(T)$, in its SER state, is denoted by GHSER_i, i.e.,

$$\mathrm{GHSER}_i = {}^0G_i^{\phi}(T) - H_i^{\mathrm{SER}}(298.15\ \mathrm{K}) \tag{2}$$

In the present work, the Gibbs energy functions for elements are taken from the SGTE compilation of Dinsdale [23].

4.2. Solution phases

In the Cr–Sn–Ti system, there are four solution phases: liquid, hcp, bct and bcc, their molar Gibbs energies are described by the following expression:

$$G_m^{\phi} = x_{\mathrm{Cr}}G_{\mathrm{Cr}}^{\phi}(T) + x_{\mathrm{Sn}}G_{\mathrm{Sn}}^{\phi}(T) + x_{\mathrm{Ti}}G_{\mathrm{Ti}}^{\phi}(T) + RT(x_{\mathrm{Cr}}\ln x_{\mathrm{Cr}} + x_{\mathrm{Sn}}\ln x_{\mathrm{Sn}} + x_{\mathrm{Ti}}\ln x_{\mathrm{Ti}}) + {}^{E}G_m^{\phi} \tag{3}$$

where R is the gas constant; x_{Cr}, x_{Sn} and x_{Ti} are the mole fractions of the pure elements Cr, Sn and Ti, respectively; ${}^{E}G_m^{\phi}$ is the excess Gibbs energy, expressed by the Redlich–Kister–Muggianu polynomial [24,25],

$$\begin{aligned}{}^{E}G_m^{\phi} &= x_{\mathrm{Cr}}x_{\mathrm{Sn}}\sum_j {}^{j}L_{\mathrm{Cr,Sn}}^{\phi}(x_{\mathrm{Cr}} - x_{\mathrm{Sn}})^j + x_{\mathrm{Cr}}x_{\mathrm{Ti}}\sum_j {}^{j}L_{\mathrm{Cr,Ti}}^{\phi}(x_{\mathrm{Cr}} - x_{\mathrm{Ti}})^j \\ &\quad + x_{\mathrm{Sn}}x_{\mathrm{Ti}}\sum_j {}^{j}L_{\mathrm{Sn,Ti}}^{\phi}(x_{\mathrm{Sn}} - x_{\mathrm{Ti}})^j + x_{\mathrm{Cr}}x_{\mathrm{Sn}}x_{\mathrm{Ti}}L_{\mathrm{Cr,Sn,Ti}}^{\phi}\end{aligned} \tag{4}$$

where ${}^{j}L_{\mathrm{Cr,Sn}}^{\phi}$, ${}^{j}L_{\mathrm{Cr,Ti}}^{\phi}$ and ${}^{j}L_{\mathrm{Sn,Ti}}^{\phi}$ are the binary interaction parameters between elements Cr and Sn, Cr and Ti, and Sn and Ti, respectively. Its general form is

$$L^{\phi} = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} \tag{5}$$

but in most case only the first one or two terms are used according to the temperature dependence of the experimental data. $L_{\mathrm{Cr,Sn,Ti}}^{\phi}$ is the ternary interaction parameter and is expressed as:

$$L_{\mathrm{Cr,Sn,Ti}}^{\phi} = x_{\mathrm{Cr}}{}^{0}L_{\mathrm{Cr,Sn,Ti}}^{\phi} + x_{\mathrm{Sn}}{}^{1}L_{\mathrm{Cr,Sn,Ti}}^{\phi} + x_{\mathrm{Ti}}{}^{2}L_{\mathrm{Cr,Sn,Ti}}^{\phi} \tag{6}$$

where ${}^{j}L_{\mathrm{Cr,Sn,Ti}}^{\phi} = a_j + b_jT$, a_j and b_j are the parameters to be optimized in this work.

4.3. Intermetallic compounds

The compounds $\mathrm{Sn_3Ti_2}$, $\mathrm{Sn_5Ti_6}$ and $\mathrm{Sn_3Ti_5}$ were treated as line compounds $\mathrm{Sn}_m\mathrm{Ti}_n$ by a two-sublattice model $(\mathrm{Sn})_m(\mathrm{Cr,Ti})_n$ in the Cr–Sn–Ti system. The Gibbs energy per mole of formula unit $\mathrm{Sn}_m\mathrm{Ti}_n$ is expressed by the following equation:

$$\begin{aligned}G_m^{\mathrm{Sn}_m\mathrm{Ti}_n} &= y'_{\mathrm{Sn}}y''_{\mathrm{Ti}}G_{\mathrm{Sn:Ti}}^{\mathrm{Sn}_m\mathrm{Ti}_n} + y'_{\mathrm{Sn}}y''_{\mathrm{Cr}}G_{\mathrm{Sn:Cr}}^{\mathrm{Sn}_m\mathrm{Ti}_n} + nRT(y''_{\mathrm{Ti}}\ln y''_{\mathrm{Ti}} + y''_{\mathrm{Cr}}\ln y''_{\mathrm{Cr}}) \\ &\quad + y'_{\mathrm{Sn}}[y''_{\mathrm{Cr}}y''_{\mathrm{Ti}}\sum_j {}^{j}L_{\mathrm{Sn:Cr,Ti}}^{\mathrm{Sn}_m\mathrm{Ti}_n}(y''_{\mathrm{Cr}} - y''_{\mathrm{Ti}})^j]\end{aligned} \tag{7}$$

where y'_{*} and y''_{*} are the site fractions of Cr, Sn or Ti on the first and second sublattices, respectively; ${}^{j}L_{\mathrm{Sn:Cr,Ti}}^{\mathrm{Sn}_m\mathrm{Ti}_n}$ represents the jth interaction parameter between elements Cr and Ti on the second sublattice.

According to the crystal structure of $\mathrm{SnTi_2}$ in the Sn–Ti subsystem [21], the compound $\mathrm{SnTi_2}$ in the Cr–Sn–Ti system was treated as $(\mathrm{Sn,Va})_1(\mathrm{Cr,Ti,Va})_2$ by a two-sublattice model. The Gibbs energy per mole of formula unit $\mathrm{SnTi_2}$ is given by the following equation:

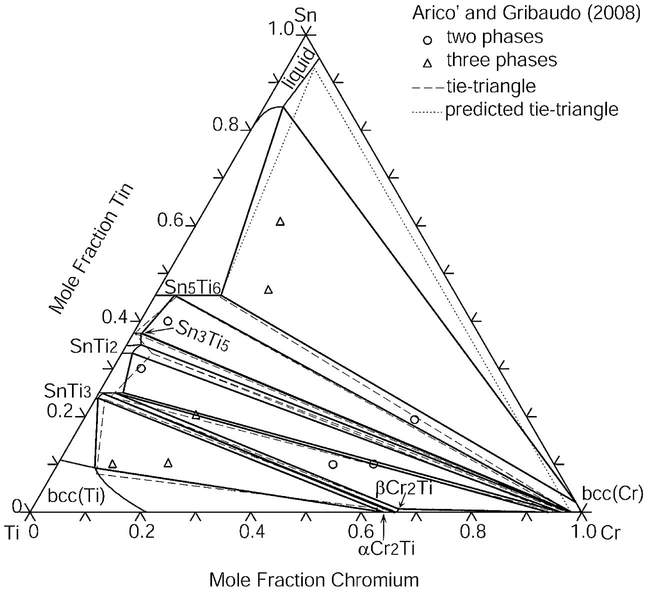

Fig. 4. Calculated isothermal section at 1173 K of the Cr–Sn–Ti system using the present thermodynamic description and comparison with the experimental data [22].

$$\begin{aligned}G_m^{\mathrm{SnTi_2}} &= y'_{\mathrm{Sn}}y''_{\mathrm{Cr}}G_{\mathrm{Sn:Cr}}^{\mathrm{SnTi_2}} + y'_{\mathrm{Sn}}y''_{\mathrm{Ti}}G_{\mathrm{Sn:Ti}}^{\mathrm{SnTi_2}} + y'_{\mathrm{Sn}}y''_{\mathrm{Va}}G_{\mathrm{Sn:Va}}^{\mathrm{SnTi_2}} + y'_{\mathrm{Va}}y''_{\mathrm{Cr}}G_{\mathrm{Va:Cr}}^{\mathrm{SnTi_2}} \\ &\quad + y'_{\mathrm{Va}}y''_{\mathrm{Ti}}G_{\mathrm{Va:Ti}}^{\mathrm{SnTi_2}} + y'_{\mathrm{Va}}y''_{\mathrm{Va}}G_{\mathrm{Va:Va}}^{\mathrm{SnTi_2}} + RT(y'_{\mathrm{Sn}}\ln y'_{\mathrm{Sn}} + y'_{\mathrm{Va}}\ln y'_{\mathrm{Va}}) \\ &\quad + 2RT(y''_{\mathrm{Cr}}\ln y''_{\mathrm{Cr}} + y''_{\mathrm{Ti}}\ln y''_{\mathrm{Ti}} + y''_{\mathrm{Va}}\ln y''_{\mathrm{Va}}) \\ &\quad + y'_{\mathrm{Sn}}[y''_{\mathrm{Cr}}y''_{\mathrm{Ti}}\sum_j {}^{j}L_{\mathrm{Sn:Cr,Ti}}^{\mathrm{SnTi_2}}(y''_{\mathrm{Cr}} - y''_{\mathrm{Ti}})^j \\ &\quad + y''_{\mathrm{Cr}}y''_{\mathrm{Va}}\sum_j {}^{j}L_{\mathrm{Sn:Cr,Va}}^{\mathrm{SnTi_2}}(y''_{\mathrm{Cr}}y''_{\mathrm{Va}})^j \\ &\quad + y''_{\mathrm{Ti}}y''_{\mathrm{Va}}\sum_j {}^{j}L_{\mathrm{Sn:Ti,Va}}^{\mathrm{SnTi_2}}(y''_{\mathrm{Ti}} - y''_{\mathrm{Va}})^j] \\ &\quad + y'_{\mathrm{Va}}[y''_{\mathrm{Cr}}y''_{\mathrm{Ti}}\sum_j {}^{j}L_{\mathrm{Sn:Cr,Ti}}^{\mathrm{SnTi_2}}(y''_{\mathrm{Cr}} - y''_{\mathrm{Ti}})^j \\ &\quad + y''_{\mathrm{Cr}}y''_{\mathrm{Va}}\sum_j {}^{j}L_{\mathrm{Sn:Cr,Va}}^{\mathrm{SnTi_2}}(y''_{\mathrm{Cr}}y''_{\mathrm{Va}})^j \\ &\quad + y''_{\mathrm{Ti}}y''_{\mathrm{Va}}\sum_j {}^{j}L_{\mathrm{Sn:Ti,Va}}^{\mathrm{SnTi_2}}(y''_{\mathrm{Ti}} - y''_{\mathrm{Va}})^j]\end{aligned}$$

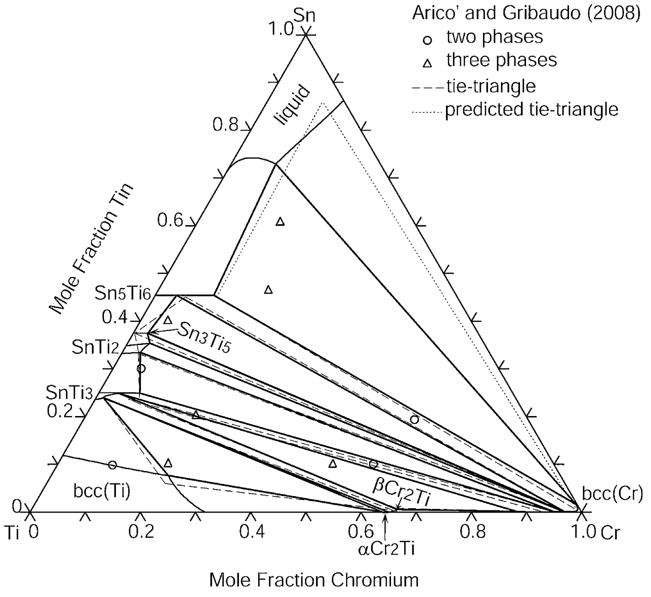

Fig. 5. Calculated isothermal section at 1373 K of the Cr–Sn–Ti system using the present thermodynamic description and comparison with the experimental data [22].

Table 1
Thermodynamic parameters in the Cr–Sn–Ti system[a].

Phase	Thermodynamic parameters		Ref.
	$\mathrm{GHSER_{Cr}}=$		[23]
	298.14–2180	$-8856.94+157.48T-26.908T\ln(T)$ $+0.00189435T^2-1.47721\times10^{-6}T^3+139250T^{-1}$	
	2180–6000	$-34869.344+344.18T-50T\ln(T)-2.88526\times10^{32}T^{-9}$	
	$\mathrm{GHSER_{Sn}}=$		[23]
	100–250	$-7958.517+122.765451T-25.858T\ln(\mathrm{T})$ $+5.1185\times10^{-4}T^2-3.192767\times10^{-6}T^3+18440T^{-1}$	
	250–505.08	$-5855.135+65.443315T-15.961T\ln(T)$ $-0.0188702T^2+3.121167\times10^{-6}T^3-61960T^{-1}$	
	505.08–800	$+2524.724+4.005269T-8.2590486T\ln(T)$ $-0.016814429T^2+2.623131\times10^{-6}T^3-1081244T^{-1}-1.2307\times10^{25}T^{-9}$	
	800–3000	$-8256.959+138.99688T-28.4512T\ln(T)-1.2307\times10^{25}T^{-9}$	
	$\mathrm{GHSER_{Ti}}=$		[23]
	298.14–900	$-8059.921+133.615208T-23.9933T\ln(T)$ $-0.004777975T^2+1.06716\times10^{-7}T^3+72636T^{-1}$	
	900–1155	$-7811.815+132.988068T-23.9887T\ln(T)$ $-0.0042033T^2-9.0876\times10^{-8}T^3+42680T^{-1}$	
	1155–1941	$+908.837+66.976538T-14.9466T\ln(T)$ $-0.0081465T^2+2.02715\times10^{-7}T^3-1477660T^{-1}$	
	1941–4000	$-124526.786+638.806871T-87.2182461T\ln(T)$ $+0.008204849T^2-3.04747\times10^{-7}T^3+36699805T^{-1}$	
Liquid	model $(\mathrm{Cr, Sn, Ti})_1$		
	$G(\mathrm{liquid, Cr})=$		[23]
	298.14–2180	$+15483.015+146.059775T-26.908T\ln(T)$ $+0.00189435T^2-1.47721\times10^{-6}T^3+139250T^{-1}+2.37615\times10^{-21}T^7$	
	2180–6000	$-16459.984+335.616316T-50T\ln(T)$	
	$G(\mathrm{liquid, Sn})=$		[23]
	100–250	$-855.425+108.677684T-25.858T\ln(T)$ $+5.1185\times10^{-4}T^2-3.192767\times10^{-6}T^3+18440T^{-1}+1.47031\times10^{-18}T^7$	
	250–505.08	$+1247.957+51.355548T-15.961T\ln(T)$ $-0.0188702T^2+3.121167\times10^{-6}T^3-61960T^{-1}+1.47031\times10^{-18}T^7$	
	505.08–800	$+9496.31-9.809114T-8.2590486T\ln(T)$ $-0.016814429T^2+2.623131\times10^{-6}T^3-1081244T^{-1}$	
	800–3000	$-1285.372+125.182498T-28.4512T\ln(T)$	
	$G(\mathrm{liquid, Ti})=$		[23]
	298.14–900	$+4134.494+126.63427T-23.9933T\ln(T)$ $-0.004777975T^2+1.06716\times10^{-7}T^3+72636T^{-1}$	
	900–1155	$+4382.601+126.00713T-23.9887T\ln(T)$ $-0.0042033T^2-9.0876\times10^{-8}T^3+42680T^{-1}$	
	1155–1300	$+13103.253+59.9956T-14.9466T\ln(T)$ $-0.0081465T^2+2.02715\times10^{-7}T^3-1477660T^{-1}$	
	1300–1941	$+369519.198-2554.0225T+342.059267T\ln(T)$ $-0.163409355T^2+1.2457117\times10^{-5}T^3-67034516T^{-1}$	
	1941–4000	$-19887.066+298.7367T-46.29T\ln(T)$	
	${}^0L^{\mathrm{liq.}}_{\mathrm{Cr,Sn}}=+55719.0-26.6540T$		[1]
	${}^1L^{\mathrm{liq.}}_{\mathrm{Cr,Sn}}=-24688.0+15.7570T$		[1]
	${}^2L^{\mathrm{liq.}}_{\mathrm{Cr,Sn}}=-6260.0-7.0780T$		[1]
	${}^0L^{\mathrm{liq.}}_{\mathrm{Cr,Ti}}=-365.8$		[12]
	${}^1L^{\mathrm{liq.}}_{\mathrm{Cr,Ti}}=-3030.2$		[12]
	${}^2L^{\mathrm{liq.}}_{\mathrm{Cr,Ti}}=+1549.1$		[12]
	${}^0L^{\mathrm{liq.}}_{\mathrm{Sn,Ti}}=-91598.9-0.9416T$		[21]
	${}^1L^{\mathrm{liq.}}_{\mathrm{Sn,Ti}}=+45682.6-12.1045T$		[21]
hcp	model $(\mathrm{Cr, Sn, Ti})_1(\mathrm{Va})_{0.5}$		
	$G(\mathrm{hcp, Cr; 0})=$		[23]
	298.14–2180	$-4418.94+157.48T-26.908T\ln(T)$ $+0.00189435T^2-1.47721\times10^{-6}T^3+139250T^{-1}$	
	2180–6000	$-30431.344+344.18T-50T\ln(T)-2.88526\times10^{32}T^{-9}$	
	Tc(hcp,Cr:Va;0) = −1109		[23]
	BMAGN(hcp,Cr:Va;0) = −2.46		[23]
	$G(\mathrm{hcp, Sn; 0})=$		[23]
	298.14–505.08	$-1955.135+57.797315T-15.961T\ln(T)$ $-0.0188702T^2+3.121167\times10^{-6}T^3-61960T^{-1}$	
	505.08–800	$+6424.724-3.640731T-8.2590486T\ln(T)$ $-0.016814429T^2+2.623131\times10^{-6}T^3-1081244T^{-1}-1.2307\times10^{25}T^{-9}$	
	800–3000	$-4356.959+131.35088T-28.4512T\ln(T)$ $-1.2307\times10^{25}T^{-9}$	
	$G(\mathrm{hcp,Ti;0})=\mathrm{GHSER_{Ti}}$		[23]
	${}^0L^{\mathrm{hcp}}_{\mathrm{Cr,Sn:Va}}=+25000.0$		[1]
	${}^0L^{\mathrm{hcp}}_{\mathrm{Cr,Ti:Va}}=+23900.0$		[12]

Table 1 (*Continued*)

Phase	Thermodynamic parameters		Ref.
	${}^{0}L^{\mathrm{hcp}}_{\mathrm{Sn,Ti:Va}} = -127549.6 + 23.2049T$		[21]
	${}^{1}L^{\mathrm{hcp}}_{\mathrm{Sn,Ti:Va}} = +64500.5 + 7.7566T$		[21]
	${}^{2}L^{\mathrm{hcp}}_{\mathrm{Sn,Ti:Va}} = +31287.6$		[21]
bcc	model $(\mathrm{Cr, Sn, Ti})_1(\mathrm{Va})_3$		
	$G(\mathrm{bcc, Cr; 0}) = \mathrm{GHSER_{Cr}}$		[23]
	Tc(bcc,Cr:Va;0) = −311.5		[23]
	BMAGN(bcc,Cr:Va;0) = −0.008		[23]
	$G(\mathrm{bcc, Sn; 0}) =$		[23]
	100–250	$-3558.517 + 116.765451T - 25.858T\ln(T)$ $+5.1185 \times 10^{-4}T^2 - 3.192767 \times 10^{-6}T^3 + 18440T^{-1}$	
	250–505.08	$-1455.135 + 59.443315T - 15.961T\ln(T)$ $-0.0188702T^2 + 3.121167 \times 10^{-6}T^3 - 61960T^{-1}$	
	505.08–800	$+6924.724 - 1.994731T - 8.2590486T\ln(T)$ $-0.016814429T^2 + 2.623131 \times 10^{-6}T^3$ $- 1081244T^{-1} - 1.2307 \times 10^{25}T^{-9}$	
	800–3000	$-3856.959 + 132.99688T - 28.4512T\ln(T)$ $-1.2307 \times 10^{25}T^{-9}$	
	$G(\mathrm{bcc, Ti; 0})=$		[23]
	298.14–1155	$-1272.064 + 134.71418T - 25.5768T\ln(T)$ $-6.63845 \times 10^{-4}T^2 - 2.78803 \times 10^{-7}T^3 + 7208T^{-1}$	
	1155–1941	$+6667.385 + 105.366379T - 22.3771T\ln(T)$ $+0.00121707T^2 - 8.4534 \times 10^{-7}\mathrm{T}^3 - 2002750T^{-1}$	
	1941–4000	$+26483.26 - 182.426471T + 19.0900905T\ln(T)$ $-0.02200832T^2 + 1.228863 \times 10^{-6}T^3 + 1400501T^{-1}$	
	${}^{0}L^{\mathrm{bcc}}_{\mathrm{Cr,Sn:Va}} = +6614.0 + 20.3770T$		[1]
	${}^{0}L^{\mathrm{bcc}}_{\mathrm{Cr,Ti:Va}} = -2247.9 + 9.1414T$		[12]
	${}^{1}L^{\mathrm{bcc}}_{\mathrm{Cr,Ti:Va}} = 198.7$		[12]
	${}^{0}L^{\mathrm{bcc}}_{\mathrm{Sn,Ti:Va}} = -142089.5 + 28.1423T$		[21]
	${}^{1}L^{bcc}_{Sn,Ti:Va} = +41211.5$		[21]
	${}^{0}L^{\mathrm{bcc}}_{\mathrm{Cr,Sn,Ti}} = -289453.3$		This work
	${}^{1}L^{\mathrm{bcc}}_{\mathrm{Cr,Sn,Ti}} = +43044.9$		This work
	${}^{2}L^{\mathrm{bcc}}_{\mathrm{Cr,Sn,Ti}} = -46850.9$		This work
bct	model $(\mathrm{Sn, Ti})_1$		
	$G(\mathrm{bct, Sn; 0}) = \mathrm{GHSER_{Sn}}$		[23]
	$G(\mathrm{bct, Ti; 0})=$		[23]
	298.14–900	$-3457.721 + 133.615208T - 23.9933T\ln(T)$ $-0.004777975T^2 + 1.06716 \times 10^{-7}T^3 + 72636T^{-1}$	
	900–1155	$-3209.615 + 132.988068T - 23.9887T\ln(T)$ $-0.0042033T^2 - 9.0876 \times 10^{-8}T^3 + 42680T^{-1}$	
	1155–1941	$+5511.037 + 66.976538T - 14.9466T\ln(T)$ $-0.0081465T^2 + 2.02715 \times 10^{-7}T^3 - 1477660T^{-1}$	
	1941–3000	$-119924.586 + 638.806871T - 87.2182461T\ln(T)$ $+.008204849T^2 - 3.04747 \times 10^{-7}T^3 + 36699805T^{-1}$	
	$L^{\mathrm{bct}}_{\mathrm{Sn,Ti}} = +50000.0$		[21]
$\mathrm{Sn_3Ti_2}$	model $(\mathrm{Sn})_3(\mathrm{Cr, Ti})_2$		
	$G^{\mathrm{Sn_3Ti_2}}_{\mathrm{Sn:Cr}} = 3\mathrm{GHSER_{Sn}} + 2\mathrm{GHSER_{Cr}} + 25000.0$		This work
	$G^{\mathrm{Sn_3Ti_2}}_{\mathrm{Sn:Ti}} = 3\mathrm{GHSER_{Sn}} + 2\mathrm{GHSER_{Ti}} - 173931.8 + 7.8259T$		[21]
$\mathrm{Sn_5Ti_6}$	model $(\mathrm{Sn})_5(\mathrm{Cr, Ti})_6$		This work
	$G^{\mathrm{Sn_5Ti_6}}_{\mathrm{Sn:Cr}} = 5\mathrm{GHSER_{Sn}} + 6\mathrm{GHSER_{Cr}} + 55000.0$		This work
	$G^{\mathrm{Sn_5Ti_6}}_{\mathrm{Sn:Ti}} = 5\mathrm{GHSER_{Sn}} + 6\mathrm{GHSER_{Ti}} - 468938.3 + 5.3729T$		[21]
	${}^{0}L^{\mathrm{Sn_5Ti_6}}_{\mathrm{Sn:Cr,Ti}} = -80007.9 + 64.9107T$		This work
	${}^{1}L^{\mathrm{Sn_5Ti_6}}_{\mathrm{Sn:Cr,Ti}} = +269730.8$		This work
$\mathrm{SnTi_3}$	model $(\mathrm{Sn, Va})_1(\mathrm{Cr, Ti})_3$		
	$G^{\mathrm{SnTi_3}}_{\mathrm{Sn:Cr}} = \mathrm{GHSER_{Sn}} + 3\mathrm{GHSER_{Cr}} + 20000.0$		This work
	$G^{\mathrm{SnTi_3}}_{\mathrm{Sn:Ti}} = \mathrm{GHSER_{Sn}} + 3\mathrm{GHSER_{Ti}} - 141133.1 + 1.1272T$		[21]
	$G^{\mathrm{SnTi_3}}_{\mathrm{Va:Cr}} = 3\mathrm{GHSER_{Cr}} + 15000.0$		This work
	$G^{\mathrm{SnTi_3}}_{\mathrm{Va:Ti}} = 3\mathrm{GHSER_{Ti}} + 15000.0$		[21]
	${}^{0}L^{\mathrm{SnTi_3}}_{\mathrm{Sn:Cr,Ti}} = +10002.3 - 15.0054T$		This work
$\mathrm{SnTi_2}$	model $(\mathrm{Sn, Va})_1(\mathrm{Cr, Ti, Va})_2$		
	$G^{\mathrm{SnTi_2}}_{\mathrm{Sn:Cr}} = \mathrm{GHSER_{Sn}} + 2\mathrm{GHSER_{Cr}} + 15000.0$		This work
	$G^{\mathrm{SnTi_2}}_{\mathrm{Sn:Ti}} = \mathrm{GHSER_{Sn}} + 2\mathrm{GHSER_{Ti}} - 122344.8 + 6.0034T$		[21]
	$G^{\mathrm{SnTi_2}}_{\mathrm{Sn:Va}} = \mathrm{GHSER_{Sn}} + 5000.0$		[21]
	$G^{\mathrm{SnTi_2}}_{\mathrm{Va:Cr}} = 2\mathrm{GHSER_{Cr}} + 10000.0$		This work
	$G^{\mathrm{SnTi_2}}_{\mathrm{Va:Ti}} = 2\mathrm{GHSER_{Ti}} + 10000.0$		[21]
	$G^{\mathrm{SnTi_2}}_{\mathrm{Va:Va}} = +300000.0$		[21]
	${}^{0}L^{\mathrm{SnTi_2}}_{\mathrm{Sn,Va:Ti}} = -34085.2$		[21]
	${}^{0}L^{\mathrm{SnTi_2}}_{\mathrm{Sn:Ti,Va}} = -49803.9 + 24.4710T$		[21]
	${}^{0}L^{\mathrm{SnTi_2}}_{\mathrm{Sn:Cr,Ti}} = -30006.2 + 15.0571T$		This work
$\mathrm{Sn_3Ti_5}$	model $(\mathrm{Sn})_3(\mathrm{Cr, Ti})_5$		
	$G^{\mathrm{Sn_3Ti_5}}_{\mathrm{Sn:Cr}} = 3\mathrm{GHSER_{Sn}} + 5\mathrm{GHSER_{Cr}} + 40000.0$		This work

Table 1 (*Continued*)

Phase	Thermodynamic parameters	Ref.
	$G^{Sn_3Ti_5}_{Sn:Ti} = 3GHSER_{Sn} + 5GHSER_{Ti} - 330186.5 + 5.3066T$	[21]
	${}^{0}L^{Sn_3Ti_5}_{Sn:Cr,Ti} = -16050.0 - 13.0000T$	This work
αCr_2Ti	model $(Cr, Sn, Ti)_2(Cr, Sn, Ti)_1$	
	$G^{\alpha Cr_2Ti}_{Cr:Cr} = 3GHSER_{Cr} + 15000.0$	[12]
	$G^{\alpha Cr_2Ti}_{Cr:Sn} = 2GHSER_{Cr} + GHSER_{Sn} + 15000.0$	This work
	$G^{\alpha Cr_2Ti}_{Cr:Ti} = 2GHSER_{Cr} + GHSER_{Ti} - 29567.6 + 7.5577T$	[12]
	$G^{\alpha Cr_2Ti}_{Sn:Cr} = 2GHSER_{Sn} + GHSER_{Cr} + 15000.0$	This work
	$G^{\alpha Cr_2Ti}_{Sn:Sn} = 3GHSER_{Sn} + 15000.0$	This work
	$G^{\alpha Cr_2Ti}_{Sn:Ti} = 2GHSER_{Sn} + GHSER_{Ti} + 15000.0$	This work
	$G^{\alpha Cr_2Ti}_{Ti:Cr} = 2GHSER_{Ti} + GHSER_{Cr} + 29567.6 - 7.5577T$	[12]
	$G^{\alpha Cr_2Ti}_{Ti:Sn} = 2GHSER_{Ti} + GHSER_{Sn} - 122344.8 + 6.0034T$	[21]
	$G^{\alpha Cr_2Ti}_{Ti:Ti} = 3GHSER_{Ti} + 15000.0$	[12]
	${}^{0}L^{\alpha Cr_2Ti}_{Cr,Ti:Cr} = {}^{0}L^{\alpha Cr_2Ti}_{Cr,Ti:Ti} = +21340.6 + 13.5420T$	[12]
	${}^{0}L^{\alpha Cr_2Ti}_{Cr:Cr,Ti} = {}^{0}L^{\alpha Cr_2Ti}_{Ti:Cr,Ti} = +50000.0$	[12]
	${}^{0}L^{\alpha Cr_2Ti}_{Sn,Ti:Cr} = {}^{0}L^{\alpha Cr_2Ti}_{Cr:Sn,Ti} = -60000.0$	This work
	${}^{0}L^{\alpha Cr_2Ti}_{Cr,Sn:Ti} = {}^{0}L^{\alpha Cr_2Ti}_{Ti:Cr,Sn} = -55000.0$	This work
βCr_2Ti	model $(Cr, Sn, Ti)_2(Cr, Sn, Ti)_1$	
	$G^{\beta Cr_2Ti}_{Cr:Cr} = 3GHSER_{Cr} + 15000.0$	[12]
	$G^{\beta Cr_2Ti}_{Cr:Sn} = 2GHSER_{Cr} + GHSER_{Sn} + 15000.0$	This work
	$G^{\beta Cr_2Ti}_{Cr:Ti} = 2GHSER_{Cr} + GHSER_{Ti} - 28472.8 + 6.5185T$	[12]
	$G^{\beta Cr_2Ti}_{Sn:Cr} = 2GHSER_{Sn} + GHSER_{Cr} + 15000.0$	This work
	$G^{\beta Cr_2Ti}_{Sn:Sn} = 3GHSER_{Sn} + 15000.0$	This work
	$G^{\beta Cr_2Ti}_{Sn:Ti} = 2GHSER_{Sn} + GHSER_{Ti} + 15000.0$	This work
	$G^{\beta Cr_2Ti}_{Ti:Cr} = 2GHSER_{Ti} + GHSER_{Cr} + 28472.8 - 6.5185T$	[12]
	$G^{\beta Cr_2Ti}_{Ti:Sn} = 2GHSER_{Ti} + GHSER_{Sn} - 122344.8 + 6.0034T$	[21]
	$G^{\beta Cr_2Ti}_{Ti:Ti} = 3GHSER_{Ti} + 15000.0$	[12]
	${}^{0}L^{\beta Cr_2Ti}_{Cr,Ti:Cr} = {}^{0}L^{\beta Cr_2Ti}_{Cr,Ti:Ti} = +50000.0$	[12]
	${}^{0}L^{\beta Cr_2Ti}_{Cr:Cr,Ti} = {}^{0}L^{\beta Cr_2Ti}_{Ti:Cr,Ti} = +60000.0$	[12]
	${}^{0}L^{\beta Cr_2Ti}_{Sn,Ti:Cr} = {}^{0}L^{\beta Cr_2Ti}_{Cr:Sn,Ti} = -60000.0$	This work
	${}^{0}L^{\beta Cr_2Ti}_{Cr,Sn:Ti} = {}^{0}L^{\beta Cr_2Ti}_{Ti:Cr,Sn} = -55000.0$	This work
γCr_2Ti	model $(Cr, Sn, Ti)_2(Cr, Sn, Ti)_1$	
	$G^{\gamma Cr_2Ti}_{Cr:Cr} = 3GHSER_{Cr} + 15000.0$	[12]
	$G^{\gamma Cr_2Ti}_{Cr:Sn} = 2GHSER_{Cr} + GHSER_{Sn} + 15000.0$	This work
	$G^{\gamma Cr_2Ti}_{Cr:Ti} = 2GHSER_{Cr} + GHSER_{Ti} - 26611.8 + 5.3142T$	[12]
	$G^{\gamma Cr_2Ti}_{Sn:Cr} = 2GHSER_{Sn} + GHSER_{Cr} + 15000.0$	This work
	$G^{\gamma Cr_2Ti}_{Sn:Sn} = 3GHSER_{Sn} + 15000.0$	This work
	$G^{\gamma Cr_2Ti}_{Sn:Ti} = 2GHSER_{Sn} + GHSER_{Ti} + 15000.0$	This work
	$G^{\gamma Cr_2Ti}_{Ti:Cr} = 2GHSER_{Ti} + GHSER_{Cr} + 26611.8 - 5.3142T$	[12]
	$G^{\gamma Cr_2Ti}_{Ti:Sn} = 2GHSER_{Ti} + GHSER_{Sn} - 122344.8 + 6.0034T$	[21]
	$G^{\gamma Cr_2Ti}_{Ti:Ti} = 3GHSER_{Ti} + 15000.0$	[12]
	${}^{0}L^{\gamma Cr_2Ti}_{Cr,Ti:Cr} = {}^{0}L^{\gamma Cr_2Ti}_{Cr,Ti:Ti} = +50000.0$	[12]
	${}^{0}L^{\gamma Cr_2Ti}_{Cr:Cr,Ti} = {}^{0}L^{\gamma Cr_2Ti}_{Ti:Cr,Ti} = +60000.0$	[12]
	${}^{0}L^{\gamma Cr_2Ti}_{Cr:Cr,Ti} = {}^{0}L^{\gamma Cr_2Ti}_{Ti:Cr,Ti} = +60000.0$	[12]

[a] In J/mol of the formula units.

$$+y'_{Sn}y'_{Va}[y''_{Cr}\sum_{j} {}^{j}L^{SnTi_2}_{Sn,Va:Cr}(y'_{Sn}-y'_{Va})^{j}$$

$$+y''_{Ti}\sum_{j} {}^{j}L^{SnTi_2}_{Sn,Va:Ti}(y'_{Sn}-y'_{Va})^{j}+y''_{Va}\sum_{j} {}^{j}L^{SnTi_2}_{Sn,Va:Va}(y'_{Sn}-y'_{Va})^{j}] \qquad (8)$$

The compound $SnTi_3$ was treated as the formula $(Sn, Va)_1(Cr, Ti)_3$ by a two-sublattice model in the Cr–Sn–Ti system. The Gibbs energy per mole of formula unit $SnTi_3$ is expressed by the following equation:

$$G^{SnTi_3}_{m} = y'_{Sn}y''_{Cr}G^{SnTi_3}_{Sn:Cr} + y'_{Sn}y''_{Ti}G^{SnTi_3}_{Sn:Ti} + y'_{Va}y''_{Cr}G^{SnTi_3}_{Va:Cr} + y'_{Va}y''_{Ti}G^{SnTi_3}_{Va:Ti}$$

$$+RT(y'_{Sn}\ln y'_{Sn}+y'_{Va}\ln y'_{Va})+3RT(y''_{Cr}\ln y''_{Cr}+y''_{Ti}\ln y''_{Ti})$$

$$+y'_{Sn}y'_{Va}[y''_{Cr}\sum_{j} {}^{j}L^{SnTi_3}_{Sn,Va:Cr}(y'_{Sn}-y'_{Va})^{j}$$

Table 2

Calculated invariant reactions in the Cr–Sn–Ti system.

Reaction	Type	*T* (K)	Liquid compositions		
			x(Cr)	*x*(Sn)	*x*(Ti)
liq + bcc(Ti) + bcc(Cr)	C_1	1790	0.5535	0.1044	0.3421
liq + bcc(Ti) → bcc(Cr) + $SnTi_3$	U_1	1779	0.3016	0.2301	0.4683
liq + Sn_3Ti_5 → Sn_5Ti_6 + $SnTi_2$	U_2	1744	0.0679	0.3968	0.5352
liq + $SnTi_3$ → bcc(Cr) + $SnTi_2$	U_3	1728	0.1745	0.3274	0.4981
liq + $SnTi_2$ → Sn_5Ti_6 + bcc(Cr)	U_4	1714	0.1617	0.3593	0.4790
liq+ bct → Sn_5Ti_6 + bcc(Cr)	U_5	505	0.0000[a]	0.9999	0.0001
liq + Sn_5Ti_6 → Sn_3Ti_2 + bct	U_6	505	0.0000[b]	0.9999	0.0001

[a] 9.8×10^{-8}.

[b] 8.6×10^{-8}.

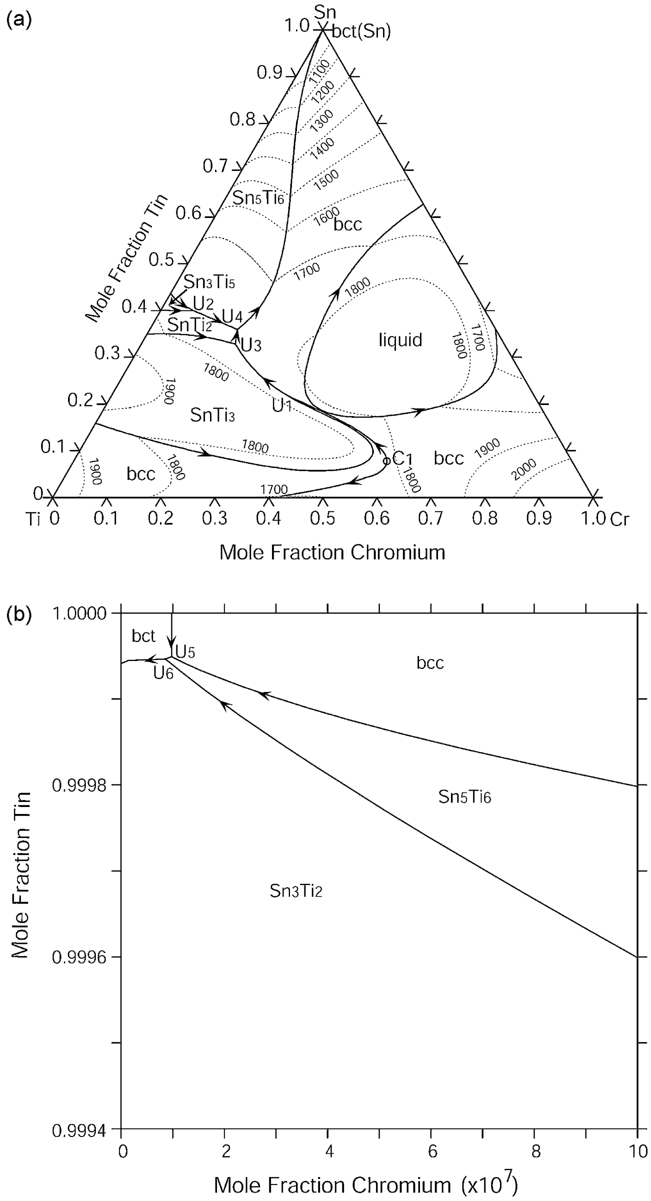

Fig. 6. (a) Calculated projection of the liquidus surfaces in the Cr–Sn–Ti system using the present thermodynamic description. (b) Enlarged section of (a).

$$+y''_{\mathrm{Ti}}\sum_j {}^jL^{\mathrm{SnTi_3}}_{\mathrm{Sn,Va:Ti}}(y'_{\mathrm{Sn}}-y'_{\mathrm{Va}})^j]$$

$$+y''_{\mathrm{Cr}}y''_{\mathrm{Ti}}[y'_{\mathrm{Sn}}\sum_j {}^jL^{\mathrm{SnTi_3}}_{\mathrm{Sn:Cr,Ti}}(y''_{\mathrm{Cr}}-y''_{\mathrm{Ti}})^j$$

$$+y'_{\mathrm{Va}}\sum_j {}^jL^{\mathrm{SnTi_3}}_{\mathrm{Va:Cr,Ti}}(y''_{\mathrm{Cr}}-y''_{\mathrm{Ti}})^j] \tag{9}$$

The compounds αCr_2Ti, βCr_2Ti and γCr_2Ti were described as a two-sublattice model $(Cr, Sn, Ti)_2(Cr, Sn, Ti)_1$ in the Cr–Sn–Ti system. The Gibbs energy per mole of formula unit Cr_2Ti is given by the following equation:

$$\begin{aligned}G^{\mathrm{Cr_2Ti}}_m &= y'_{\mathrm{Cr}}y''_{\mathrm{Cr}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Cr:Cr}}+y'_{\mathrm{Sn}}y''_{\mathrm{Cr}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Sn:Cr}}+y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Ti:Cr}}+y'_{\mathrm{Cr}}y''_{\mathrm{Sn}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Cr:Sn}}\\ &+y'_{\mathrm{Sn}}y''_{\mathrm{Sn}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Sn:Sn}}+y'_{\mathrm{Ti}}y''_{\mathrm{Sn}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Ti:Sn}}+y'_{\mathrm{Cr}}y''_{\mathrm{Ti}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Cr:Ti}}+y'_{\mathrm{Sn}}y''_{\mathrm{Ti}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Sn:Ti}}\\ &+y'_{\mathrm{Ti}}y''_{\mathrm{Ti}}G^{\mathrm{Cr_2Ti}}_{\mathrm{Ti:Ti}}+2RT(y'_{\mathrm{Cr}}\ln y'_{\mathrm{Cr}}+y'_{\mathrm{Sn}}\ln y'_{\mathrm{Sn}}+y'_{\mathrm{Ti}}\ln y'_{\mathrm{Ti}})\end{aligned}$$

$$\begin{aligned}&+RT(y''_{\mathrm{Cr}}\ln y''_{\mathrm{Cr}}+y''_{\mathrm{Sn}}\ln y''_{\mathrm{Sn}}+y''_{\mathrm{Ti}}\ln y''_{\mathrm{Ti}})\\
&+y'_{\mathrm{Cr}}y'_{\mathrm{Sn}}[y''_{\mathrm{Cr}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr,Sn:Cr}}(y'_{\mathrm{Cr}}-y'_{\mathrm{Sn}})^j\\
&+y''_{\mathrm{Sn}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr,Sn:Sn}}(y'_{\mathrm{Cr}}-y'_{\mathrm{Sn}})^j+y''_{\mathrm{Ti}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr,Sn:Ti}}(y'_{\mathrm{Cr}}-y'_{\mathrm{Sn}})^j]\\
&+y'_{\mathrm{Cr}}y'_{\mathrm{Ti}}[y''_{\mathrm{Cr}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr,Ti:Cr}}(y'_{\mathrm{Cr}}-y'_{\mathrm{Ti}})^j\\
&+y''_{\mathrm{Sn}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr,Ti:Sn}}(y'_{\mathrm{Cr}}-y'_{\mathrm{Ti}})^j+y''_{\mathrm{Ti}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr,Ti:Ti}}(y'_{\mathrm{Cr}}-y'_{\mathrm{Ti}})^j]\\
&+y'_{\mathrm{Sn}}y'_{\mathrm{Ti}}[y''_{\mathrm{Cr}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Sn,Ti:Cr}}(y'_{\mathrm{Sn}}-y'_{\mathrm{Ti}})^j\\
&+y''_{\mathrm{Sn}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Sn,Ti:Sn}}(y'_{\mathrm{Sn}}-y'_{\mathrm{Ti}})^j+y''_{\mathrm{Ti}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Sn,Ti:Ti}}(y'_{\mathrm{Sn}}-y'_{\mathrm{Ti}})^j]\\
&+y''_{\mathrm{Cr}}y''_{\mathrm{Sn}}[y'_{\mathrm{Cr}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr:Cr,Sn}}(y''_{\mathrm{Cr}}y''_{\mathrm{Sn}})^j+y'_{\mathrm{Sn}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Sn:Cr,Sn}}(y''_{\mathrm{Cr}}y''_{\mathrm{Sn}})^j\\
&+y'_{\mathrm{Ti}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Ti:Cr,Sn}}(y''_{\mathrm{Cr}}y''_{\mathrm{Sn}})^j]+y''_{\mathrm{Cr}}y''_{\mathrm{Ti}}[y'_{\mathrm{Cr}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr:Cr,Ti}}(y''_{\mathrm{Cr}}-y''_{\mathrm{Ti}})^j\\
&+y'_{\mathrm{Sn}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Sn:Cr,Ti}}(y''_{\mathrm{Cr}}-y''_{\mathrm{Ti}})^j+y'_{\mathrm{Ti}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Ti:Cr,Ti}}(y''_{\mathrm{Cr}}-y''_{\mathrm{Ti}})^j]\\
&+y''_{\mathrm{Sn}}y''_{\mathrm{Ti}}[y'_{\mathrm{Cr}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr:Sn,Ti}}(y''_{\mathrm{Sn}}y''_{\mathrm{Ti}})^j\\
&+y'_{\mathrm{Sn}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Sn:Sn,Ti}}(y''_{\mathrm{Sn}}y''_{\mathrm{Ti}})^j+y'_{\mathrm{Ti}}\sum_j {}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Ti:Sn,Ti}}(y''_{\mathrm{Sn}}y''_{\mathrm{Ti}})^j]\end{aligned} \tag{10}$$

Because the values of solubility of Sn in the Laves phases αCr_2Ti and βCr_2Ti is small (∼1.2 at.% at 1373 K) [22], in the present work, the ternary interaction parameters ${}^jL^{\mathrm{Cr_2Ti}}_{*:\mathrm{Cr,Sn,Ti}}$ and ${}^jL^{\mathrm{Cr_2Ti}}_{\mathrm{Cr,Sn,Ti}:*}$ were not optimized and listed in the Eq. (10).

5. Assessment procedure

A careful examination of existing thermodynamic descriptions of the Cr–Sn [1], Cr–Ti [12] and Sn–Ti [21] sub-systems is made.

A general rule for selection of the adjustable parameters is that only those coefficients related to the experimental results should be adjusted [26]. The optimization is carried out by means of the optimization module PARROT of the thermodynamic software Thermo-Calc [27,28], which can handle various kinds of experimental data.

The thermodynamic parameters for the Cr–Sn–Ti system are optimized on the basis of the experimental information available in the literature [22].

For the liquid, bct, bcc and hcp solution phases, the parameters ${}^0L^{\mathrm{liq.}}_{\mathrm{Cr,Sn}}$, ${}^1L^{\mathrm{liq.}}_{\mathrm{Cr,Sn}}$, ${}^2L^{\mathrm{liq.}}_{\mathrm{Cr,Sn}}$, ${}^0L^{\mathrm{bcc}}_{\mathrm{Cr,Sn}}$, ${}^1L^{\mathrm{bcc}}_{\mathrm{Cr,Sn}}$ and ${}^0L^{\mathrm{bct}}_{\mathrm{Cr,Sn}}$ in the Cr–Sn sub-system [1], ${}^0L^{\mathrm{liq.}}_{\mathrm{Cr,Ti}}$, ${}^1L^{\mathrm{liq.}}_{\mathrm{Cr,Ti}}$, ${}^0L^{\mathrm{bcc}}_{\mathrm{Cr,Ti}}$, ${}^1L^{\mathrm{bcc}}_{\mathrm{Cr,Ti}}$ and ${}^0L^{\mathrm{hcp}}_{\mathrm{Cr,Ti}}$ in the Cr–Ti sub-system [12], ${}^0L^{\mathrm{liq.}}_{\mathrm{Sn,Ti}}$, ${}^1L^{\mathrm{liq.}}_{\mathrm{Sn,Ti}}$, ${}^0L^{\mathrm{bcc}}_{\mathrm{Sn,Ti}}$, ${}^1L^{\mathrm{bcc}}_{\mathrm{Sn,Ti}}$, ${}^0L^{\mathrm{hcp}}_{\mathrm{Sn,Ti}}$, ${}^1L^{\mathrm{hcp}}_{\mathrm{Sn,Ti}}$, ${}^2L^{\mathrm{hcp}}_{\mathrm{Sn,Ti}}$, ${}^0L^{\mathrm{bct}}_{\mathrm{Sn,Ti}}$ in the Sn–Ti sub-system [21] are used, and only three ternary interaction parameters ${}^0L^{\mathrm{bcc}}_{\mathrm{Cr,Sn,Ti}}$, ${}^1L^{\mathrm{bcc}}_{\mathrm{Cr,Sn,Ti}}$ and ${}^2L^{\mathrm{bcc}}_{\mathrm{Cr,Sn,Ti}}$ in the bcc solution were optimized in this work based on the experimental data [22]. The experimental information about the liquidus and other thermodynamic properties in liquid mixture is very scarce, so the ternary interaction parameters of liquid phase in the Cr–Sn–Ti system were not optimized.

For the compounds Sn_3Ti_2, Sn_5Ti_6 and Sn_3Ti_5 in the Cr–Sn–Ti system, the parameters $G^{Sn_3Ti_2}_{Sn:Cr}$, $G^{Sn_5Ti_6}_{Sn:Cr}$, $G^{Sn_3Ti_5}_{Sn:Cr}$ are fixed to a positive value +5000 J/mol of atoms relative to the mechanical mixture of the two nearest-neighboring stable structures in a corresponding proportion according to the estimation of Fernandez Guillermet and Huang [29] for high melting bcc metals V, Nb and Ta. The parameters $G^{Sn_3Ti_2}_{Sn:Ti}$, $G^{Sn_5Ti_6}_{Sn:Ti}$, $G^{Sn_3Ti_5}_{Sn:Ti}$ are taken from the description of the corresponding binary Sn–Ti sub-system [21]. Because stable Sn_3Ti_2 cannot be found at 1173 and 1373 K in the Cr–Sn–Ti system [22], the parameters ${}^{j}L^{Sn_3Ti_2}_{Sn:Cr,Ti}$ are not optimized in this work. The parameters ${}^{0}L^{Sn_5Ti_6}_{Sn:Cr,Ti}$, ${}^{1}L^{Sn_5Ti_6}_{Sn:Cr,Ti}$ and ${}^{0}L^{Sn_3Ti_5}_{Sn:Cr,Ti}$ are optimized according to the experimental data [22].

For the $SnTi_2$ compound, the parameter $G^{SnTi_2}_{Sn:Cr}$ and $G^{SnTi_2}_{Va:Cr}$ are fixed to a positive value +5000 J/mol of atoms relative to the mechanical mixture of the pure elements in a corresponding proportion. The parameters $G^{SnTi_2}_{Sn:Ti}$, $G^{SnTi_2}_{Va:Ti}$, $G^{SnTi_2}_{Sn:Va}$, $G^{SnTi_2}_{Va:Va}$, ${}^{0}L^{SnTi_2}_{Sn,Va:Ti}$ and ${}^{0}L^{SnTi_2}_{Sn:Ti,Va}$ are taken from the existing thermodynamic description of the Sn–Ti system [21]. In the present work, ${}^{0}L^{SnTi_2}_{Sn:Cr,Ti}$ is optimized according to the experimental data [22].

For the $SnTi_3$ compound, the parameters $G^{SnTi_3}_{Sn:Cr}$ and $G^{SnTi_3}_{Va:Cr}$ are fixed to a positive value +5000 J/mol of atoms relative to the mechanical mixture of the two nearest-neighboring stable structures in a corresponding proportion. The parameters $G^{SnTi_3}_{Sn:Ti}$ and $G^{SnTi_3}_{Va:Ti}$ are taken from the thermodynamic description of the Sn–Ti sub-system [21]. The interaction parameter ${}^{0}L^{SnTi_3}_{Sn:Cr,Ti}$ is optimized according to the experimental data [22].

For the compounds αCr_2Ti, βCr_2Ti and γCr_2Ti, the parameters $G^{Cr_2Ti}_{Cr:Sn}$, $G^{Cr_2Ti}_{Sn:Cr}$, $G^{Cr_2Ti}_{Sn:Sn}$ and $G^{Cr_2Ti}_{Sn:Ti}$ are fixed to a positive value +5000 J/mol of atoms relative to the mechanical mixture of the pure elements in a corresponding proportion according to the estimation of Fernandez Guillermet and Huang [29] for high melting bcc metals V, Nb and Ta. The parameters $G^{Cr_2Ti}_{Cr:Cr}$, $G^{Cr_2Ti}_{Cr:Ti}$, $G^{Cr_2Ti}_{Ti:Cr}$, $G^{Cr_2Ti}_{Ti:Ti}$, ${}^{0}L^{Cr_2Ti}_{Cr,Ti:Cr}$, ${}^{0}L^{Cr_2Ti}_{Cr,Ti:Ti}$, ${}^{0}L^{Cr_2Ti}_{Cr:Cr,Ti}$, ${}^{0}L^{Cr_2Ti}_{Ti:Cr,Ti}$ and $G^{Cr_2Ti}_{Ti:Sn}$ are taken from the thermodynamic description of the corresponding binary Cr–Ti [12] and Sn–Ti [21] sub-systems. The parameters ${}^{0}L^{\alpha Cr_2Ti}_{Sn,Ti:Cr}$, ${}^{0}L^{\alpha Cr_2Ti}_{Cr:Sn,Ti}$, ${}^{0}L^{\beta Cr_2Ti}_{Sn,Ti:Cr}$, ${}^{0}L^{\beta Cr_2Ti}_{Cr:Sn,Ti}$ are optimized to be −60,000 J/mol of the formula units according to experimental data [22]. The parameters ${}^{0}L^{\alpha Cr_2Ti}_{Cr,Sn:Ti}$, ${}^{0}L^{\alpha Cr_2Ti}_{Ti:Cr,Sn}$, ${}^{0}L^{\beta Cr_2Ti}_{Cr,Sn:Ti}$, ${}^{0}L^{\beta Cr_2Ti}_{Ti:Cr,Sn}$ are optimized to be −55,000 J/mol of the formula units according to experimental data [22].

6. Results and calculations

The thermodynamic descriptions of the Cr–Sn–Ti system obtained in the present work are shown in Table 1.

Figs. 1–3 present the calculated Cr–Sn, Cr–Ti and Sn–Ti phase diagrams using the thermodynamic description of Jerlerud Pérez and Sundman [1], Ghosh [12] and Yin et al. [21], respectively.

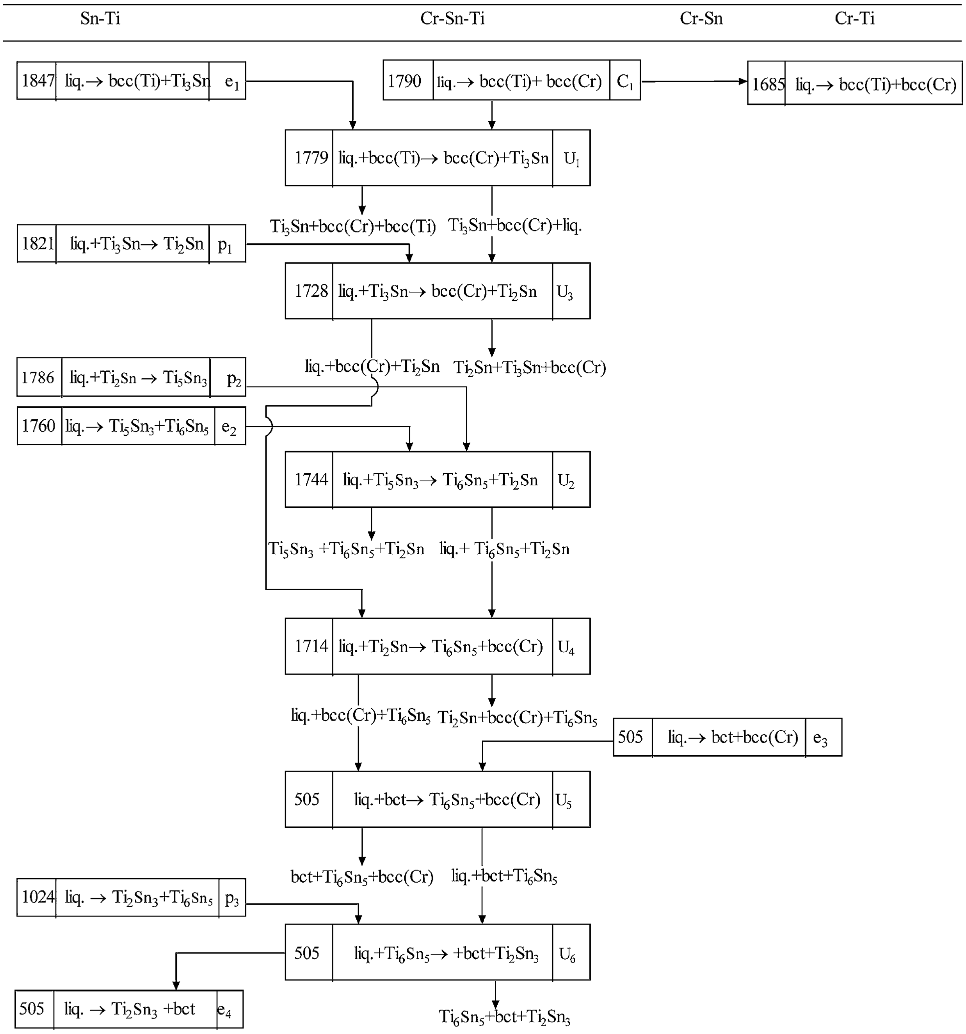

Fig. 7. Predicted reaction scheme related to liquid of the Cr–Sn–Ti system.

Figs. 4 and 5 show the calculated isothermal section at 1173 and 1373 K, respectively, in the Cr–Sn–Ti system by the present thermodynamic description, and comparison with the experimental data determined by Aricó and Gribaudo [22]. The calculated results are similar to the experiments [22]. There are several differences between the calculated results and experimental data [22]. Firstly, the three-phase region bcc (Cr) + αCr_2Ti (βCr_2Ti?) + $SnTi_3$ was replaced by two three-phase fields of $\alpha Cr_2Ti + \beta Cr_2Ti + SnTi_3$ and bcc (Cr) + $\beta Cr_2Ti + SnTi_3$, because αCr_2Ti and βCr_2Ti are stable at 1173 and 1373 K in the Sn–Ti binary sub-system [21]. Secondly, although Aricó and Gribaudo [22] identified only two-phase assemblages $SnTi_2$ and $SnTi_3$, Sn_5Ti_6 and bcc(Cr), and αCr_2Ti and $SnTi_3$ in the specimens 7–9 (5.1%Cr-30.1% Sn-64.9% Ti, 5.0% Cr-40.0% Sn-55.0% Ti and 49.9% Cr-10.0% Sn-40.1% Ti) at 1173 K, respectively, using the optical microscopy, SEM and XRD, these alloys were located in three-phase regions $SnTi_3 + SnTi_2$ + bcc(Cr), $Sn_3Ti_5 + Sn_5Ti_6$ + bcc(Cr) and bcc(Cr)+ $\alpha Cr_2Ti + SnTi_3$ in the constructed isothermal section, which is agreement with the present work. Thirdly, in order to reproduce the relationship of two three-phase regions $Sn_3Ti_5 + Sn_5Ti_6$ + bcc(Cr) and $Sn_3Ti_5 + SnTi_2$ + bcc(Cr), Sn_3Ti_5 is optimized to have a considerable solubility of chromium in the present work. Otherwise, three-phase region $Sn_3Ti_5 + SnTi_2 + Sn_5Ti_6$ will appear. Finally, The calculated composition of the liquid phase in three-phase region liquid + Sn_5Ti_6 + bcc(Cr) is different to the tie-triangle predicted by Aricó and Gribaudo [22].

Fig. 6 is the predicted projection of the liquidus surfaces of the Cr–Sn–Ti system according to the present thermodynamic description. There is a big liquids valley in the projection section, which is adjusted and effected strongly by the interaction parameter of liquid, ${}^{0}L^{\text{liq.}}_{\text{Cr,Sn,Ti}}$. Further experimental work, such as the liquidus or vertical sections in this composition range, need to be done. The calculated invariant reactions in the Cr–Sn–Ti system are listed in Table 2.

Fig. 7 shows the predicted reaction scheme related to liquid in the Cr–Sn–Ti system on the basis of the calculated results using the present thermodynamic description.

7. Summary

The phase relations and thermodynamic descriptions in the Cr–Sn–Ti system are critically evaluated from the experimental information available in the literatures. A set of self-consistent thermodynamic parameters describing the Gibbs energy of each individual phase as a function of composition and temperature was derived. The projection of the liquidus surfaces and the reaction scheme related to liquid of the Cr–Sn–Ti system have been established. With the thermodynamic description available, one can now make various thermodynamic calculations of practical interest in the Cr–Sn–Ti ternary alloy system.

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