Journal of Alloys and Compounds 509 (2011) 1936–1946

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Thermodynamic modeling of the Ti–Al–Cr ternary system

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ARTICLE INFO

Article history:
Received 14 July 2010
Received in revised form 9 October 2010
Accepted 21 October 2010
Available online 30 October 2010

Keywords:
Ti–Al–Cr
Calphad
Titanium alloys

ABSTRACT

The Ti–Al–Cr ternary system is one of the most important systems to studying the titanium alloys. Some experimental data of this ternary system are available and a few partial thermodynamic assessments are reported. However, no full thermodynamic descriptions were published. In this study, the previous work on the Ti–Al–Cr system and its related binary systems are reviewed. Based on the thermodynamic descriptions of the Ti–Al, Ti–Cr and Al–Cr systems and the ternary experimental data in literature, the Ti–Al–Cr ternary system is assessed by means of the Calphad method. Several isothermal sections from 1073 K to 1573 K and some invariant reactions are calculated, which are in good agreement with the most of the experimental results.

1. Introduction

The phase diagram of the Ti–Al–Cr ternary system is fundamental to developing the novel structural and functional alloys containing these elements. γ-TiAl based alloys are considered as the candidate materials for elevated temperature applications, engineering materials in the aviation and automotive industry, for their numerous advantages such as low density, good oxidation resistance, and attractive high temperature property, they have been widely studied in the latest years [1–9]. The studies of structure and some properties of Ti–Cr alloys and the formation of nanocomposites containing Al and $TiAl_3$ in Ti–Al alloys are also reported in recent years [10–12]. In additon, the Ti–Al based coatings including Cr for high temperature oxidation protection of γ-TiAl are also investigated recently [13–15]. Furthermore, Cr is the common β-stabilizer for the titanium alloys [16], and much cheaper than the elements V, Mo and Nb [17–18]. Therefore, it is essential to study the phase relationship in the Ti–Al–Cr system.

The experimental phase diagram of the Ti–Al–Cr system was first reported by Busch in 1950s [19]. Today, several sets of experimental data of this ternary system are available and some assessments are also reported. However, no full thermodynamic description has been published.

In this study, the available thermodynamic data for the three binary systems (Ti–Al, Ti–Cr and Al–Cr) [20–22] are reviewed. Then, the thermodynamic parameters of the Ti–Al–Cr system are optimized, including the one for the new ternary compound $L1_2$_$Ti_{25}Cr_8Al_{67}$, the ternary interaction parameters of bcc_a2 and B2, hcp, liquid and some interaction parameters involving the third element (for example, the interaction between the element Al and Cr in γ-TiAl). Finally, several sectional phase diagrams from 1073 K to 1573 K and the invariant reaction temperatures are presented.

2. Review of the literature information

2.1. Binary systems

Several thermodynamic descriptions of the Ti–Al system are available [20,23–24]. However, the one newly assessed by Witusiewicz et al. [20] is in good agreement with the latest experimental results and is adopted in this work.

The Ti–Cr system was recently assessed by Ghosh [21], Murray [25], Chen et al. [26] and Zhuang [27]. The phase boundaries and the activity of Cr at 1653 K in bcc phase calculated by Ghosh [21] are in good agreement with the latest experimental results [28]. Thus, Ghosh's thermodynamic parameters are accepted in this work.

The latest assessments of the Al–Cr system was reported by Chen et al. [22] and Liang et al. [29]. Considering the compatibility when extrapolating into the Ti–Al–Cr–Mn-X multi-component system, the models of γ_2_αAl_8Cr_5 and γ_1_βAl_8Cr_5 were treated as $(Al,Cr)_{12}(Al,Cr)_5(Al,Cr)_9$ and $(Al,Cr)_{17}(Al,Cr)_9$, respectively, by Chen et al. [22], which is used in the current Ti–Al–Cr ternary system.

2.2. Ti–Al–Cr ternary system

The experimental results of this ternary system reported before 1990 were reviewed by Hayes in 1992 [30]. Some Ti-rich corner isothermal sections presented by Hayes in the temperature range of 873–1473 K are mainly based on the experimental results obtained by Ence et al. in 1960s [31]. In recent decades, more attentions are

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doi:10.1016/j.jallcom.2010.10.092

paid to the phase equilibria of the Ti-rich corner from 1073 K to 1573 K. Recently, Raghavan [32] and Bochvar et al. [33] reviewed the updated experimental results on the phase equilibria. Gros et al. [34], Shao and Tsakiropoulos [35] and Kaufman [36] calculated this system by the Calphad method, however, no details of modeling were reported in their publications.

2.2.1. *The experimental data of Ti–Al–Cr at Ti-rich corner*

Early in 1988, Gros et al. studied the Ti-rich corner of the isothermal section of Ti–Al–Cr system at 1073 K and calculated this isothermal section by the Calphad method [34]. Most of their calculated results are in agreement with the experimental results obtained by Jewett in 1997 [37], particularly in the existence of the three-phase field αTi + βTi + Ti_3Al. In contrast with Jewett's experimental results, Gros et al. did not consider the existence of B2 phase in their calculation. In order to verify the existence of $L1_2$_$Ti_{25}Cr_8Al_{67}$, the Al–30 at% Ti–15 at% Cr alloy was heat-treated in air at 1273 K and 1073 K for 100 h and cooled in air for 5 min [38], Brady et al. concluded that the compound $L1_2$_$Ti_{25}Cr_8Al_{67}$ is stable at 1273 K and decomposes at 1073 K. However, Jewett et al.'s updated studies [37,39–41] deny Brady et al.'s experimental conclusions.

In 1997, Jewett [37] summarized the previous experimental results in detail and reviewed the experimental studies presented in 1992 by Hayes [30]. In addition, Jewett also studied the γ-TiAl region by SEM/EDX (standardless) method [37]. The latest experimental data at 1073 K reported by Jewett in 1997 is applied in this work.

Little experimental result at 1173 K was reported. Recently, Chen et al. studied this isothermal section by XRD-EDX and obtained the related tie-lines and tie-triangles [42]. There are lots of reports on the isothermal section at 1273 K at Ti-rich corner [30,37,39–40,43–47]. In 1990s, Hayes [30] and Mabuchi et al. [43] reviewed the early experimental studies at 1273 K. More studies [37,39–40,45–47] were published recently.

The C14, γ-TiAl region was studied by Jewett et al. in 1995–1997 [37,39–40]. Their early work in 1995–1996 was mainly focused on the C14 and it was concluded that the solubility of Al in C14 was about 40 at% in 1073 K and 1273 K [39–40]. In 1997, the γ-TiAl region was studied by SEM/EDX and the related tie-lines and tie-triangles were obtained [37].

Later, Kainuma et al. further studied the Ti-rich corner at 1273 K by the TEM, EDS, EMPA and also reported the related tie-lines and tie-triangles [45–46]. Fujita et al. analyzed the phase equilibrium relationship by XRD method in 2001 [47]. The experimental results at 1273 K reported by Jewett, Kainuma et al. and Fujita et al. are taken into account in this work.

The isothermal section at 1473 K was reported by Kainuma et al. [46], Fujita et al. [47] and Hashimoto [48] recently, Kainuma et al. quantitatively studied the Ti–Al boundary (30–60 at% Al) by EPMA method and reported the related tie-lines and tie-triangles [46]. Later Fujita et al. [47] and Hashimoto [48] deduced the approximate phase equilibrium relationship at Ti-rich corner by XRD method and their results are in partial agreement with Kainuma et al.'s results. However they still debated whether C14 exists in this region, Fujita et al. doubted the existence of C14, while Hashimoto reported the contrary opinion.

Little information on the isothermal section at 1573 K was reported. In 2000, Kainuma et al. studied the Ti–Al boundary (30–60 at% Al) at 1573 K by EPMA method and reported the related tie-lines and tie-triangles [46], which are directly adopted in this work.

The only experimental data for thermodynamic values were obtained by Jacobson et al. [49]

2.2.2. *The experimental data of Ti–Al–Cr at Al-rich corner*

The experimental results at Al-rich corner were scarcely reported. Available studies in literature are summarized as follows: Jewett et al. studied the Al-rich corner at 1073 K and 1273 K in 1996 [41,50]. The isothermal section at 1423 K was studied by Nayakama et al. [51], Park et al. [52], Mabuchi et al. [53] and the one at 1473 K was studied by Klansky et al. [54]. There exist a lot of uncertainties at the isothermal section at 1073 K reported by Jewett et al. and at 1473 K reported by Klansky et al. Since this work mainly focuses on the Ti-rich corner, only the isothermal sections at 1273 K and 1423 K are calculated and compared with the experimental ones. Jewett et al.'s results reported at 1273 K in 1996 [41] are in significant difference from Nakayama et al.'s [51], however, he pointed out that Nakayama et al.'s experimental alloys did not reach equilibrium. Therefore, we comply Jewett et al.'s results and neglect Nakayama et al.'s results in this work.

2.2.3. *Invariant equilibria*

The confirmed invariant reactions at the Ti-rich corner are shown in Eqs. (1)–(4).

$$\text{liquid} + \alpha\text{Ti} = \beta\text{Ti} + \gamma\text{-TiAl} \tag{1}$$

$$\text{liquid} + \gamma\text{-TiAl} = \beta\text{Ti} + L1_2\_Ti_{25}Cr_8Al_{67} \tag{2}$$

$$\alpha\text{Ti} + \gamma\text{-TiAl} = \beta\text{Ti} + Ti_3Al \tag{3}$$

$$\gamma\text{-TiAl} + L1_2\_Ti_{25}Cr_8Al_{67} = \text{C14} + TiAl_2 \tag{4}$$

Recently, Bochvar et al. [33] reviewed a series of experimental data and Chen et al. [42] studied these reactions. The temperature ranges of these reactions were reported as follows: 1623–1763 K [33] for reaction (1), about 1573 K [33] or 1583 K [42] for reaction (2), 1273–1392 K [33] for reaction (3) and 1073–1273 K [33] for reaction (4).

At Al-rich corner, the confirmed reactions are the following:

$$\text{liquid} + \beta = \beta Al_8Cr_5 + L1_2\_Ti_{25}Cr_8Al_{67} \tag{5}$$

$$\text{liquid} + Ti_2Al_5 = L1_2\_Ti_{25}Cr_8Al_{67} + \text{H\_}TiAl_3 \tag{6}$$

The temperature ranges of these reactions are: 1513 K [33] or 1533 K [42] for reaction (5) and 1603 K [33] for reaction (6).

There is an uncertainty about the formation of the $L1_2$_$Ti_{25}Cr_8Al_{67}$ phase. Bochvar et al. [33] reported that the $L1_2$_$Ti_{25}Cr_8Al_{67}$ phase formed peritectically from liquid + γ-TiAl + Ti_2Al_5 at 1623 K, while Chen et al. [42] doubted that this phase formed at 1645 K from the reaction as follows: liquid + γ-TiAl = $L1_2$_$Ti_{25}Cr_8Al_{67}$ + H_$TiAl_3$.

The reactions near the Al–Cr boundary are not taken into account in this work, because the region of the phase Al_8Cr_5 has been debated so many years in binary system Al–Cr and these ternary reactions are mostly extrapolated from the binary system Al–Cr.

3. Thermodynamic modeling and parameters optimization

3.1. *Unary phases*

The Gibbs free energy function for the element i (i = Ti, Al and Cr) in the phase Ø (Ø = liquid, bcc, fcc, etc.) is described by Eq. (7).

$$^0G_i^{\varnothing}(T) = a + bT + cT\ln T + dT^2 + e/T + \ldots \tag{7}$$

In the present work, the Gibbs free energy functions are taken from the SGTE compilation of Dinsdale [55].

3.2. *Solution phases*

In the Ti–Al–Cr ternary system, there exist several solution phases, such as the liquid, bcc and hcp. Their Gibbs free energies are described by the following expression:

$$^{0}G^{\text{Ø}} = \sum_i x_i {}^{0}G_i^{\text{Ø}} + RT\sum_i x_i \ln x_i + G^E \tag{8}$$

where x_i is the mole fraction of component i, ${}^{0}G_i^{\varnothing}$ is the Gibbs free energy of the pure component i with structure Ø, R is the gas constant and T is the absolute temperature. G^E is the excess Gibbs free energy of the phase which is defined as:

$$G^E = \sum_{i,j=1(i\neq j)}^{n} x_i x_j \sum_{k=0}^{m} L_{(i,j)}^{k}(x_i - x_j)^k + \sum_{i,j,l=1(i\neq j\neq l)}^{n} x_i x_j x_l \sum_{k=i,j,l} L_k V_k \tag{9}$$

where, the first term represents the binary interaction terms, the second one represents the ternary interactions. $L_{(i,j)}^{k}$'s are the binary interaction parameters for the i–j binary and L_k's are the ternary interaction parameters. V_k is defined as: $V_k = x_k + \dfrac{1-\sum_{p=i,j,l} x_p}{n}$

3.3. Intermetallic compounds

In the Ti–Al–Cr ternary system, there exist many intermetallic compounds, including the Laves phases, Ti_3Al, γ-TiAl, $TiAl_2$, $TiAl_3$, Ti_2Al_5, γ_1_βAl_8Cr_5, γ_2_αAl_8Cr_5 and $L1_2$_$Ti_{25}Cr_8Al_{67}$. In the modeling of most of the intermediate phases, we use models where not all elements appear on all sublattices, because the model of the intermediate phases is mainly extrapolated from the sub-binary systems, and these models are directly taken from the recent description of these phases [33,39–40,56–61]. For each intermetallic compound, the model will be discussed in detail later. The Gibbs free energy of each compound can be described by the following expression:

$$G^{\text{Ø}} = {}^{\text{ref}}G^{\text{Ø}} + {}^{\text{id}}G^{\text{Ø}} + {}^{\text{E}}G^{\text{Ø}} \tag{10}$$

The model of the Laves phases is taken as $(Al,Cr,Ti)_2(Cr,Ti)$, which is based on the model of $TiCr_2$ in the Ti–Cr system and the studies of Jewett et al. in 1995–1996 [39–40]. The terms ${}^{\text{ref}}G^{\text{Ø}}$, ${}^{\text{id}}G^{\text{Ø}}$ and ${}^{\text{E}}G^{\text{Ø}}$ for the Laves phases can be expressed by Eqs. (11)–(15), respectively:

$$\begin{aligned}{}^{\text{ref}}G^{\text{Ø}} = {} & y'_{Cr}y''_{Cr}G^{\text{Ø}}_{Cr:Cr} + y'_{Ti}y''_{Ti}G^{\text{Ø}}_{Ti:Ti} + y'_{Al}y''_{Cr}G^{\text{Ø}}_{Al:Cr} + y'_{Al}y''_{Ti}G^{\text{Ø}}_{Al:Ti} + \\ & y'_{Cr}y''_{Ti}G^{\text{Ø}}_{Cr:Ti} + y'_{Ti}y''_{Cr}G^{\text{Ø}}_{Ti:Cr}\end{aligned} \tag{11}$$

$${}^{\text{id}}G^{\text{Ø}} = 2RT(y'_{Al}\ln y'_{Al} + y'_{Cr}\ln y'_{Cr} + y'_{Ti}\ln y'_{Ti}) + RT(y''_{Cr}\ln y''_{Cr} + y''_{Ti}\ln y''_{Ti}) \tag{12}$$

$$\begin{aligned}{}^{\text{E}}G^{\text{Ø}}_{C14} = {} & y'_{Cr}y''_{Cr}y''_{Ti}L^0_{Cr:Cr,Ti} + y'_{Ti}y''_{Cr}y''_{Ti}L^0_{Ti:Cr,Ti} + y'_{Cr}y'_{Ti}y''_{Cr}L^0_{Cr,Ti:Cr} + y'_{Cr}y'_{Ti}y''_{Ti}L^0_{Cr,Ti:Ti} \\ & + y'_{Al}y'_{Cr}y''_{Ti}L^0_{Al,Cr:Ti} + y'_{Al}y'_{Cr}y''_{Ti}(y'_{Al} - y'_{Cr})L^1_{Al,Cr:Ti} + y'_{Al}y'_{Ti}y''_{Ti}L^0_{Al,Ti:Ti}\end{aligned} \tag{13}$$

$$\begin{aligned}{}^{\text{E}}G^{\text{Ø}}_{C36} = {} & y'_{Cr}y''_{Cr}y''_{Ti}L^0_{Cr:Cr,Ti} + y'_{Ti}y''_{Cr}y''_{Ti}L^0_{Ti:Cr,Ti} + y'_{Cr}y'_{Ti}y''_{Cr}L^0_{Cr,Ti:Cr} + y'_{Cr}y'_{Ti}y''_{Ti}L^0_{Cr,Ti:Ti} \\ & + y'_{Al}y'_{Cr}y''_{Ti}L^0_{Al,Cr:Ti}\end{aligned} \tag{14}$$

$${}^{\text{E}}G^{\text{Ø}}_{C15} = y'_{Cr}y''_{Cr}y''_{Ti}L^0_{Cr:Cr,Ti} + y'_{Ti}y''_{Cr}y''_{Ti}L^0_{Ti:Cr,Ti} + y'_{Cr}y'_{Ti}y''_{Cr}L^0_{Cr,Ti:Cr} + y'_{Cr}y'_{Ti}y''_{Ti}L^0_{Cr,Ti:Ti} \tag{15}$$

The Ti_3Al is modeled as $(Al,Cr,Ti)_3(Al,Ti)$ in the ternary system, which is based on the substitution of Cr for Ti in Ti_3Al confirmed by Hao et al. [56]. Its ${}^{\text{ref}}G^{\text{Ø}}$, ${}^{\text{id}}G^{\text{Ø}}$, and ${}^{\text{E}}G^{\text{Ø}}$ can be described by the following expressions:

$$\begin{aligned}{}^{\text{ref}}G^{\text{Ø}} = {} & y'_{Al}y''_{Al}G^{\text{Ø}}_{Al:Al} + y'_{Ti}y''_{Ti}G^{\text{Ø}}_{Ti:Ti} + y'_{Al}y''_{Ti}G^{\text{Ø}}_{Al:Ti} + y'_{Cr}y''_{Al}G^{\text{Ø}}_{Cr:Al} + \\ & y'_{Cr}y''_{Ti}G^{\text{Ø}}_{Cr:Ti} + y'_{Ti}y''_{Cr}G^{\text{Ø}}_{Ti:Cr}\end{aligned} \tag{16}$$

$${}^{\text{id}}G^{\text{Ø}} = 3RT(y'_{Al}\ln y'_{Al} + y'_{Cr}\ln y'_{Cr} + y'_{Ti}\ln y'_{Ti}) + RT(y''_{Al}\ln y''_{Al} + y''_{Ti}\ln y''_{Ti}) \tag{17}$$

$${}^{\text{E}}G^{\text{Ø}} = y'_{Al}y'_{Ti}y''_{Al}L^0_{Al,Ti:Al} + y'_{Ti}y''_{Al}y''_{Ti}L^0_{Ti:Al,Ti} + y'_{Cr}y'_{Ti}y''_{Al}L^0_{Cr,Ti:Al} \tag{18}$$

The γ-TiAl is modeled as (Al,Cr,Ti) (Al,Cr,Ti) in the ternary system, which is based on the site selectivity of Cr in γ-TiAl studied by Hao et al. [56] and Wolf et al. [57]. Wolf et al. reported that Cr mainly substitutes for Al site [57]. However, Hao et al. believed that Cr occupies both Ti and Al sites with approximately equal probability, and Cr prefers the Ti sites and further increases with increasing Al or Cr contents [56]. The ${}^{\text{ref}}G^{\text{Ø}}$, ${}^{\text{id}}G^{\text{Ø}}$, and ${}^{\text{E}}G^{\text{Ø}}$ of γ-TiAl can be described by the following expressions:

$$\begin{aligned}{}^{\text{ref}}G^{\text{Ø}} = {} & y'_{Al}y''_{Al}G^{\text{Ø}}_{Al:Al} + y'_{Cr}y''_{Cr}G^{\text{Ø}}_{Cr:Cr} + y'_{Ti}y''_{Ti}G^{\text{Ø}}_{Ti:Ti} + y'_{Al}y''_{Cr}G^{\text{Ø}}_{Al:Cr} + \\ & y'_{Al}y''_{Ti}G^{\text{Ø}}_{Al:Ti} + y'_{Cr}y''_{Al}G^{\text{Ø}}_{Cr:Al} + y'_{Cr}y''_{Ti}G^{\text{Ø}}_{Cr:Ti} + y'_{Ti}y''_{Cr}G^{\text{Ø}}_{Ti:Cr} + y'_{Ti}y''_{Cr}G^{\text{Ø}}_{Ti:Cr}\end{aligned} \tag{19}$$

$$\begin{aligned}{}^{\text{id}}G^{\text{Ø}} = {} & RT(y'_{Al}\ln y'_{Al} + y'_{Cr}\ln y'_{Cr} + y'_{Ti}\ln y'_{Ti}) \\ & + RT(y''_{Al}\ln y''_{Al} + y''_{Cr}\ln y''_{Cr} + y''_{Ti}\ln y''_{Ti})\end{aligned} \tag{20}$$

$$\begin{aligned}{}^{\text{E}}G^{\text{Ø}} = {} & y'_{Al}y'_{Ti}y''_{Al}(L^0_{Al,Ti:Al} + (y'_{Al} - y'_{Ti})L^1_{Al,Ti:Al} + (y'_{Al} - y'_{Ti})^2 L^2_{Al,Ti:Al}) \\ & y'_{Al}y''_{Al}y''_{Ti}(L^0_{Al:Al,Ti} + (y''_{Al} - y''_{Ti})L^1_{Al:Al,Ti} + (y''_{Al} - y''_{Ti})^2 L^2_{Al:Al,Ti}) \\ & + y'_{Al}y'_{Ti}y''_{Ti}L^0_{Al,Ti:Ti} + y'_{Ti}y''_{Al}y''_{Ti}L^0_{Ti:Al,Ti} + y'_{Al}y'_{Cr}y''_{Ti}L^0_{Al,Cr:Ti} + y'_{Al}y''_{Cr}y''_{Ti}L^0_{Al:Cr,Ti}\end{aligned} \tag{21}$$

The models of $TiAl_2$, $TiAl_3$ and Ti_2Al_5 are taken as $(Al,Cr,Ti)_m(Al,Ti)_n$ in the ternary system. There are no reports of the crystal structure of the related ternary phases containing the third element Cr. However, the solubilities of Cr in these phases are very small at a series of experimental isothermal sections [33]. Therefore, it is reasonable to assume that the element Cr mainly substitutes for the Al site. The terms ${}^{\text{ref}}G^{\text{Ø}}$, ${}^{\text{id}}G^{\text{Ø}}$, and ${}^{\text{E}}G^{\text{Ø}}$ for these phases can be described by the following expressions:

$$\begin{aligned}{}^{\text{ref}}G^{\text{Ø}} = {} & y'_{Al}y''_{Al}{}^{0}G^{\text{Ø}}_{Al:Al} + y'_{Ti}y''_{Al}{}^{0}G^{\text{Ø}}_{Ti:Al} + y'_{Al}y''_{Ti}{}^{0}G^{\text{Ø}}_{Al:Ti} \\ & + y'_{Ti}y''_{Ti}{}^{0}G^{\text{Ø}}_{Ti:Ti} + y'_{Cr}y''_{Al}{}^{0}G^{\text{Ø}}_{Cr:Al} + y'_{Cr}y''_{Ti}{}^{0}G^{\text{Ø}}_{Cr:Ti}\end{aligned} \tag{22}$$

$$\begin{aligned}{}^{\text{id}}G^{\text{Ø}} = {} & mRT(y'_{Al}\ln y'_{Al} + y'_{Cr}\ln y'_{Cr} + y'_{Ti}\ln y'_{Ti}) \\ & + nRT(y''_{Al}\ln y''_{Al} + y''_{Ti}\ln y''_{Ti})\end{aligned} \tag{23}$$

$$\begin{aligned}{}^{\text{E}}G^{\text{Ø}} = {} & y'_{Al}y'_{Ti}y''_{Al}L^0_{Al,Ti:Al} + y'_{Al}y'_{Ti}y''_{Ti}L^0_{Al,Ti:Ti} + y'_{Al}y''_{Al}y''_{Ti}L^0_{Al:Al,Ti} \\ & + y'_{Ti}y''_{Al}y''_{Ti}L^0_{Ti:Al,Ti} + y'_{Al}y'_{Cr}y''_{Ti}L^0_{Al,Cr:Ti}\end{aligned} \tag{24}$$

The model of γ_1_βAl_8Cr_5 is taken as $(Al,Cr,Ti)_{17}(Al,Ti)_9$ in the ternary system, this model is mainly extrapolated from the Al–Cr system assessed recently [22], the calculated results are in good agreement with the most experimental results. In order to simplify the model, when extrapolating into the Ti–Al–Cr–Mn-X multicomponent system, it may be more reasonable to use the two sublattices. It is also based on the isothermal section at 1423 K reported by Mabuchi et al. [53], in his work, he pointed that the Cr content was fixed when Ti adds to this compound. The terms ${}^{\text{ref}}G^{\text{Ø}}$, ${}^{\text{id}}G^{\text{Ø}}$, and ${}^{\text{E}}G^{\text{Ø}}$ of γ_1_βAl_8Cr_5 can be described by the following expressions:

$$\begin{aligned}{}^{\text{ref}}G^{\text{Ø}} = {} & y'_{Al}y''_{Cr}{}^{0}G^{\text{Ø}}_{Al:Cr} + y'_{Cr}y''_{Al}{}^{0}G^{\text{Ø}}_{Cr:Al} + y'_{Al}y''_{Al}{}^{0}G^{\text{Ø}}_{Al:Al} + \\ & y'_{Cr}y''_{Cr}{}^{0}G^{\text{Ø}}_{Cr:Cr} + y'_{Ti}y''_{Cr}{}^{0}G^{\text{Ø}}_{Ti:Cr} + y'_{Ti}y''_{Al}{}^{0}G^{\text{Ø}}_{Ti:Al}\end{aligned} \tag{25}$$

$$\begin{aligned}{}^{\text{id}}G^{\text{Ø}} = {} & 17RT(y'_{Al}\ln y'_{Al} + y'_{Cr}\ln y'_{Cr} + y'_{Ti}\ln y'_{Ti}) \\ & + 9RT(y''_{Al}\ln y''_{Al} + y''_{Cr}\ln y''_{Cr})\end{aligned} \tag{26}$$

$$\begin{aligned}{}^{\text{E}}G^{\text{Ø}} = {} & y'_{Al}y''_{Al}y''_{Cr}L^0_{Al:Al,Cr} + y'_{Cr}y''_{Al}y''_{Cr}L^0_{Cr:Al,Cr} + \\ & y'_{Al}y'_{Cr}y''_{Al}L^0_{Al,Cr:Al} + y'_{Al}y'_{Cr}y''_{Al}(y'_{Al} - y'_{Cr})L^1_{Al,Cr:Al} + \\ & y'_{Al}y'_{Cr}y''_{Cr}L^0_{Al,Cr:Cr} + y'_{Al}y'_{Cr}y''_{Cr}(y'_{Al} - y'_{Cr})L^1_{Al,Cr:Cr} + \\ & y'_{Al}y'_{Ti}y''_{Cr}L^0_{Al,Ti:Cr} + y'_{Ti}y''_{Al}y''_{Cr}L^0_{Ti:Al,Cr}\end{aligned} \tag{27}$$

Table 1
Thermodynamic parameters of Ti-Al-Cr system.

Phase	Parameter (in J/mol)
Liquid	$^{0}L^{\mathrm{liquid}}_{\mathrm{Al,Cr,Ti}} = -32,000$
bcc	$^{0}L^{\mathrm{bcc}}_{\mathrm{Al,Cr,Ti}} = 94,230 - 10 \times T$
	$^{1}L^{\mathrm{bcc}}_{\mathrm{Al,Cr,Ti}} = -100,000$
	$^{2}L^{\mathrm{bcc}}_{\mathrm{Al,Cr,Ti}} = 139,216.705 - 80.99 \times T - 15 \times T \times \ln(T)$
hcp	$^{0}L^{\mathrm{hcp}}_{\mathrm{Al,Cr,Ti}} = -68,708 - 68.6 \times T$
C14	$^{0}G^{C14}_{\mathrm{Al:Ti}} = -94,500 + 20 \times T + 2 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{C14}_{\mathrm{Al:Cr}} = 10,000 + 2 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}L^{C14}_{\mathrm{Al,Cr:Ti}} = -87,025.5 - 6.5 \times T$
	$^{1}L^{C14}_{\mathrm{Al,Cr:Ti}} = 7270 + 10 \times T$
	$^{0}L^{C14}_{\mathrm{Al,Ti:Ti}} = -94,190 + 30 \times T$
C36	$^{0}G^{C36}_{\mathrm{Al:Ti}} = 2 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{C36}_{\mathrm{Al:Cr}} = 2 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}L^{C36}_{\mathrm{Al,Cr:Ti}} = -195,460 + 20 \times T$
C15	$^{0}G^{C15}_{\mathrm{Al:Ti}} = 2 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{C15}_{\mathrm{Al:Cr}} = 2 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
$\mathrm{Ti_3Al}$	$^{0}G^{\mathrm{Ti_3Al}}_{\mathrm{Cr:Ti}} = 100,000 + 3{}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Cr}} + {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{\mathrm{Ti_3Al}}_{\mathrm{Cr:Al}} = 3{}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Cr}} + {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Al}}$
	$^{0}L^{\mathrm{Ti_3Al}}_{\mathrm{Cr,Ti:Al}} = -50,000$
γ-TiAl	$^{0}G^{\gamma-\mathrm{TiAl}}_{\mathrm{Al:Cr}} = -13,000 + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Cr}}$
	$^{0}G^{\gamma-\mathrm{TiAl}}_{\mathrm{Cr:Ti}} = -8000 + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Cr}}6 + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Ti}}$
	$^{0}G^{\gamma-\mathrm{TiAl}}_{\mathrm{Ti:Cr}} = -8000 + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Ti}} + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Cr}}$
	$^{0}G^{\gamma\text{-}\mathrm{TiAl}}_{\mathrm{Cr:Cr}} = 15,000 + 2{}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Cr}}$
	$^{0}G^{\gamma\text{-}\mathrm{TiAl}}_{\mathrm{Cr:Al}} = -13,000 + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Cr}} + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}L^{\gamma\text{-}\mathrm{TiAl}}_{\mathrm{Al,Cr:Ti}} = -2000$
	$^{0}L^{\gamma\text{-}\mathrm{TiAl}}_{\mathrm{Al:Cr,Ti}} = -36,000$
$\mathrm{TiAl_2}$	$^{0}G^{\mathrm{TiAl_2}}_{\mathrm{Cr:Al}} = 2 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{TiAl_2}}_{\mathrm{Cr:Ti}} = 2 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}L^{\mathrm{TiAl_2}}_{\mathrm{Al,Cr:Ti}} = -50,000$
$\mathrm{Ti_2Al_5}$	$^{0}G^{\mathrm{Ti_2Al_5}}_{\mathrm{Cr:Al}} = 5 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 2 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{Ti_2Al_5}}_{\mathrm{Cr:Ti}} = 5 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 2 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}L^{\mathrm{Ti_2Al_5}}_{\mathrm{Al,Cr:Ti}} = -110,000$
$\mathrm{H\_TiAl_3}$	$^{0}G^{\mathrm{H\_TiAl_3}}_{\mathrm{Cr:Al}} = 3 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{H\_TiAl_3}}_{\mathrm{Cr:Ti}} = 3 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}L^{\mathrm{H\_TiAl_3}}_{\mathrm{Al,Cr:Ti}} = 80,000$
$\gamma_2\_\alpha\mathrm{Al_8Cr_5}$	$^{0}G^{\gamma_2\_\alpha\mathrm{Al_8Cr_5}}_{\mathrm{Ti:Cr:Cr}} = 50,000 + 12 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 14 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\gamma_2\_\alpha\mathrm{Al_8Cr_5}}_{\mathrm{Ti:Cr:Al}} = 12 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 5 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}6 + 9 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\gamma_2\_\alpha\mathrm{Al_8Cr_5}}_{\mathrm{Ti:Al:Cr}} = 12 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 9 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 5 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\gamma_2\_\alpha\mathrm{Al_8Cr_5}}_{\mathrm{Ti:Al:Al}} = 12 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 14 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}L^{\gamma_2\_\alpha\mathrm{Al_8Cr_5}}_{\mathrm{Al,Ti:Al:Cr}} = -680,000$
$\gamma_1\_\beta\mathrm{Al_8Cr_5}$	$^{0}G^{\gamma_1\_\beta\mathrm{Al_8Cr_5}}_{\mathrm{Ti:Cr}} = 17 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 9 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\gamma_1\_\beta\mathrm{Al_8Cr_5}}_{\mathrm{Ti:Al}} = 17 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 9 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}L^{\gamma_1\_\beta\mathrm{Al_8Cr_5}}_{\mathrm{Al,Ti:Cr}} = -326,106 - 277 \times T$
	$^{0}L^{\gamma_1\_\beta\mathrm{Al_8Cr_5}}_{\mathrm{Ti:Al,Cr}} = -1,100,000$
$\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}$	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Ti:Cr:Al}} = -33,795 + 5 \times T + 0.25 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 0.08 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 0.67 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Ti:Al:Al}} = 0.25 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 0.75 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Ti:Cr:Ti}} = 10,000 + 0.92 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 0.08 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Ti:Al:Ti}} = 0.92 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 0.08 \times {}^{0}G^{\mathrm{fcc\_a2}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Ti:Cr:Cr}} = 0.25 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 0.75 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Ti:Al:Cr}} = 0.25 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}} + 0.08 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + 0.67 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Al:Cr:Al}} = 0.92 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + 0.08 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Al:Al:Al}} = {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Al:Cr:Ti}} = 0.25 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + 0.08 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 0.67 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Al:Al:Ti}} = 0.33 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + 0.67 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Al:Cr:Cr}} = 0.25 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + 0.75 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Al:Al:Cr}} = 0.33 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + 0.67 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Cr:Cr:Al}} = 0.33 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 0.67 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Cr:Al:Al}} = 0.25 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 0.75 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Cr:Cr:Ti}} = 20,000 + 0.33 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 0.67 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Cr:Al:Ti}} = 0.25 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 0.08 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}} + 0.67 \times {}^{0}G^{\mathrm{hcp\_a3}}_{\mathrm{Ti}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Cr:Cr:Cr}} = {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}}$
	$^{0}G^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Cr:Al:Cr}} = 0.92 \times {}^{0}G^{\mathrm{bcc\_a2}}_{\mathrm{Cr}} + 0.08 \times {}^{0}G^{\mathrm{fcc\_a1}}_{\mathrm{Al}}$
	$^{0}L^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Cr,Ti:Cr:Al}} = -10,000$
	$^{0}L^{\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}}_{\mathrm{Ti:Cr:Al,Ti}} = -5000$
B2	$^{0}L^{\mathrm{B2}}_{\mathrm{Ti:Cr}} = {}^{0}L^{\mathrm{B2}}_{\mathrm{Cr:Ti}} = 82,186.5 - 50.5 \times T$
	$^{0}L^{\mathrm{B2}}_{\mathrm{Ti:Al,Cr}} = {}^{0}L^{\mathrm{B2}}_{\mathrm{Al,Cr:Ti}} = 23,584 - 8 \times T$

The $\gamma_2\_\alpha\mathrm{Al_8Cr_5}$ is taken as $\mathrm{(Al,Cr,Ti)_{12}(Al,Cr)_5(Al,Cr)_9}$ in the ternary system. The terms $^{\mathrm{ref}}G^{\emptyset}$, $^{\mathrm{id}}G^{\emptyset}$, and $^{\mathrm{E}}G^{\emptyset}$ of $\gamma_2\_\alpha\mathrm{Al_8Cr_5}$ can be described by the following expressions:

$$\begin{aligned}^{\mathrm{ref}}G^{\emptyset} = {} & y'_{\mathrm{Al}}y''_{\mathrm{Al}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Al:Al:Al}} + y'_{\mathrm{Al}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Al:Al:Cr}} + y'_{\mathrm{Al}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Al:Cr:Al}} \\ & + y'_{\mathrm{Al}}y''_{\mathrm{Cr}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Al:Cr:Cr}} + y'_{\mathrm{Cr}}y''_{\mathrm{Al}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Cr:Al:Al}} + y'_{\mathrm{Cr}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Cr:Al:Cr}} \\ & + y'_{\mathrm{Cr}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Cr:Cr:Al}} + y'_{\mathrm{Cr}}y''_{\mathrm{Cr}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Cr:Cr:Cr}} + y'_{\mathrm{Ti}}y''_{\mathrm{Al}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Ti:Al:Al}} \\ & + y'_{\mathrm{Ti}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Ti:Al:Cr}} + y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Ti:Cr:Al}} + y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Ti:Cr:Cr}}\end{aligned} \tag{28}$$

$$\begin{aligned}^{\mathrm{id}}G^{\emptyset} = {} & 12RT(y'_{\mathrm{Al}}\ln y'_{\mathrm{Al}} + y'_{\mathrm{Cr}}\ln y'_{\mathrm{Cr}} + y'_{\mathrm{Ti}}\ln y'_{\mathrm{Ti}}) \\ & + 5RT(y''_{\mathrm{Al}}\ln y''_{\mathrm{Al}} + y''_{\mathrm{Cr}}\ln y''_{\mathrm{Cr}}) \\ & + 9RT(y'''_{\mathrm{Al}}\ln y'''_{\mathrm{Al}} + y'''_{\mathrm{Cr}}\ln y'''_{\mathrm{Cr}})\end{aligned} \tag{29}$$

$$\begin{aligned}^{\mathrm{E}}G^{\emptyset} = {} & y'_{\mathrm{Al}}y'_{\mathrm{Cr}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}L^{0}_{\mathrm{Al,Cr:Al:Cr}} + y'_{\mathrm{Al}}y'_{\mathrm{Cr}}y''_{\mathrm{Al}}y'''_{\mathrm{Al}}L^{0}_{\mathrm{Al,Cr:Al:Al}} \\ & + y'_{\mathrm{Al}}y'_{\mathrm{Ti}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}L^{0}_{\mathrm{Al,Ti:Al:Cr}}\end{aligned} \tag{30}$$

The new ternary compound $\mathrm{L_{12}\_Ti_{25}Cr_8Al_{67}}$ is modeled as $\mathrm{(Al,Cr,Ti)_{0.25}(Al,Cr)_{0.08}(Al,Cr,Ti)_{0.67}}$ in the ternary system, which is based on the Zhang et al. [58], Nic et al. [59–60] and Kogachi et al.'s results [61], in which the $\mathrm{L_{12}}$ ternary compound is the "$\mathrm{TiAl_3}$-based" intermetallic and the element Cr occupies both Ti and Al sites. The terms for Gibbs free energy of this phase can be described by the following expressions:

$$\begin{aligned}^{\mathrm{ref}}G^{\emptyset} = {} & y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Ti:Cr:Al}} + y'_{\mathrm{Ti}}y''_{\mathrm{Al}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Ti:Al:Al}} + y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}y'''_{\mathrm{Ti}}G^{\emptyset}_{\mathrm{Ti:Cr:Ti}} \\ & + y'_{\mathrm{Ti}}y''_{\mathrm{Al}}y'''_{\mathrm{Ti}}G^{\emptyset}_{\mathrm{Ti:Al:Ti}} + y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Ti:Cr:Cr}} + y'_{\mathrm{Ti}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Ti:Al:Cr}} \\ & + y'_{\mathrm{Al}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Al:Cr:Al}} + y'_{\mathrm{Al}}y''_{\mathrm{Al}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Al:Al:Al}} + y'_{\mathrm{Al}}y''_{\mathrm{Cr}}y'''_{\mathrm{Ti}}G^{\emptyset}_{\mathrm{Al:Cr:Ti}} \\ & + y'_{\mathrm{Al}}y''_{\mathrm{Al}}y'''_{\mathrm{Ti}}G^{\emptyset}_{\mathrm{Al:Al:Ti}} + y'_{\mathrm{Al}}y''_{\mathrm{Cr}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Al:Cr:Cr}} + y'_{\mathrm{Al}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Al:Al:Cr}} \\ & + y'_{\mathrm{Cr}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Cr:Cr:Al}} + y'_{\mathrm{Cr}}y''_{\mathrm{Al}}y'''_{\mathrm{Al}}G^{\emptyset}_{\mathrm{Cr:Al:Al}} + y'_{\mathrm{Cr}}y''_{\mathrm{Cr}}y'''_{\mathrm{Ti}}G^{\emptyset}_{\mathrm{Cr:Cr:Ti}} \\ & + y'_{\mathrm{Cr}}y''_{\mathrm{Al}}y'''_{\mathrm{Ti}}G^{\emptyset}_{\mathrm{Cr:Al:Ti}} + y'_{\mathrm{Cr}}y''_{\mathrm{Cr}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Cr:Cr:Cr}} + y'_{\mathrm{Cr}}y''_{\mathrm{Al}}y'''_{\mathrm{Cr}}G^{\emptyset}_{\mathrm{Cr:Al:Cr}}\end{aligned} \tag{31}$$

$$^{\mathrm{E}}G^{\emptyset} = y'_{\mathrm{Cr}}y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}L^{0}_{\mathrm{Cr,Ti:Cr:Al}} + y'_{\mathrm{Ti}}y''_{\mathrm{Cr}}y'''_{\mathrm{Al}}y'''_{\mathrm{Ti}}L^{0}_{\mathrm{Ti:Cr:Al,Ti}} \tag{32}$$

$$\begin{aligned}^{\mathrm{id}}G^{\emptyset} = {} & 0.25RT(y'_{\mathrm{Al}}\ln y'_{\mathrm{Al}} + y'_{\mathrm{Cr}}\ln y'_{\mathrm{Cr}} + y'_{\mathrm{Ti}}\ln y'_{\mathrm{Ti}}) + 0.08RT(y''_{\mathrm{Al}}\ln y''_{\mathrm{Al}} \\ & + y''_{\mathrm{Cr}}\ln y''_{\mathrm{Cr}})0.67RT(y'''_{\mathrm{Al}}\ln y'''_{\mathrm{Al}} + y'''_{\mathrm{Cr}}\ln y'''_{\mathrm{Cr}} + y'''_{\mathrm{Ti}}\ln y'''_{\mathrm{Ti}})\end{aligned} \tag{33}$$

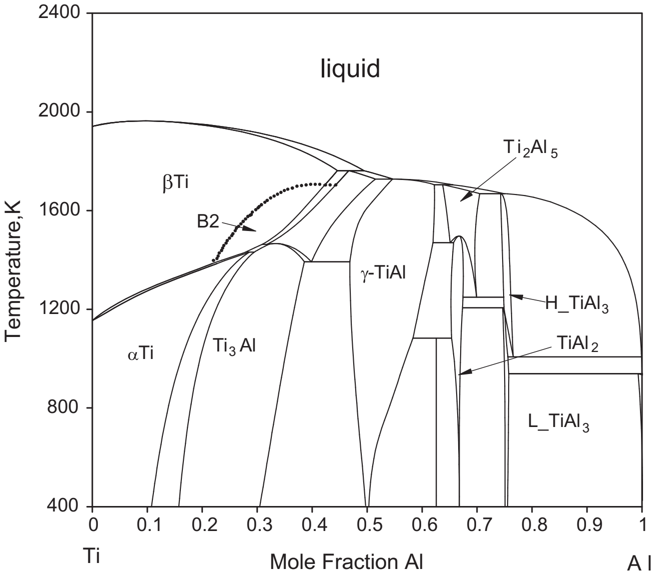

Fig. 1. The Ti–Al system assessed by Witusiewicz et al. [20].

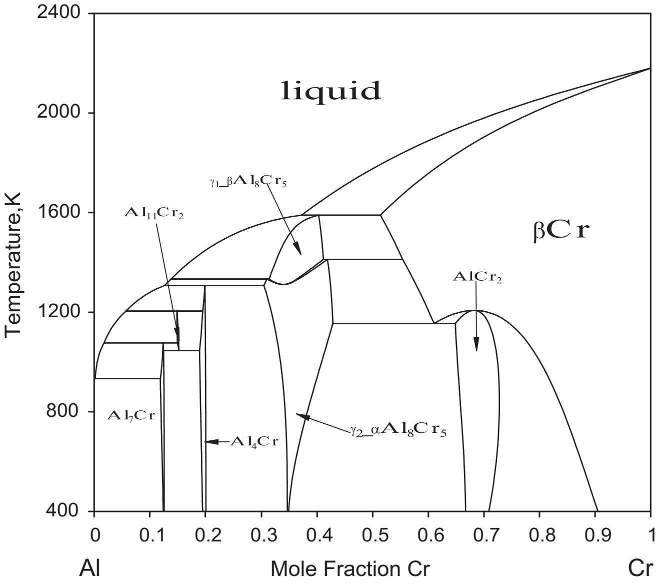

Fig. 3. The Al–Cr system assessed by Chen et al. [22].

The symbol Ø appearing in Eqs. (11)–(33) represents the Laves phases, Ti_3Al, γ-TiAl, $TiAl_2$, $TiAl_3$, Ti_2Al_5, γ_1_βAl_8Cr_5, γ_2_αAl_8Cr_5 and $L1_2$_$Ti_{25}Cr_8Al_{67}$. The parameters $y_i^{'}$, $y_i^{''}$ and $y_i^{'''}$ are the site fractions of Al, Cr or Ti on the first, second and the third sublattice, respectively. The parameter $G^{Ø}_{*:*}$ and $G^{Ø}_{*:*:*}$ represent the Gibbs free energies of the compound *ij* and *ijk*, when the first, second and the third sublattices are occupied by only one element Al, Cr or Ti, respectively. $L^0_{*:\mathrm{Cr,Ti}}$, $L^0_{\mathrm{Cr,Ti}:*}$, etc. represent the interaction parameters between the elements Cr and Ti. $L^0_{\mathrm{Al,Cr}:*}$, $L^0_{*:\mathrm{Al,Cr}:*}$, $L^0_{*:*:\mathrm{Al,Cr}}$, etc. represent the interaction parameters between the elements Al and Cr. $L^0_{\mathrm{Al,Ti}:*}$, $L^0_{*:\mathrm{Al,Ti}:*}$, $L^0_{*:*:\mathrm{Al,Ti}}$, etc. represent the interaction parameters between the elements Al and Ti.

The controversy about whether B2 phase exists in Ti–Al system lasted for many years. Based on the newly reported experimental results, Witusiewicz et al. assessed the Ti–Al system in the condition of considering B2 phase in 2008 [20]. In this work, it is considered that B2 phase in Ti–Al–Cr ternary system was extrapolated from the binary system Ti–Al, which is based on Kainuma et al.'s achievement in 2000 [45]. The phase boundaries of B2 phase reported by Kainuma et al. are in contradict with Jewett's results at 1273 K [37] and cannot be determined so far. The temperature range of B2 was still not confirmed in Bochvar et al.'s summarization [33].

4. Optimization of thermodynamic parameters

In the present work, all thermodynamic parameters are optimized by Pan-optimizer included in Pandat phase equilibrium calculation software, which is a C/C^{++} software package for evaluating thermodynamic, kinetic and thermo-physical model parameters from experimental measurements. The optimization is conducted until the sum of the squares of the errors between the calculated and the experimental thermodynamic properties and

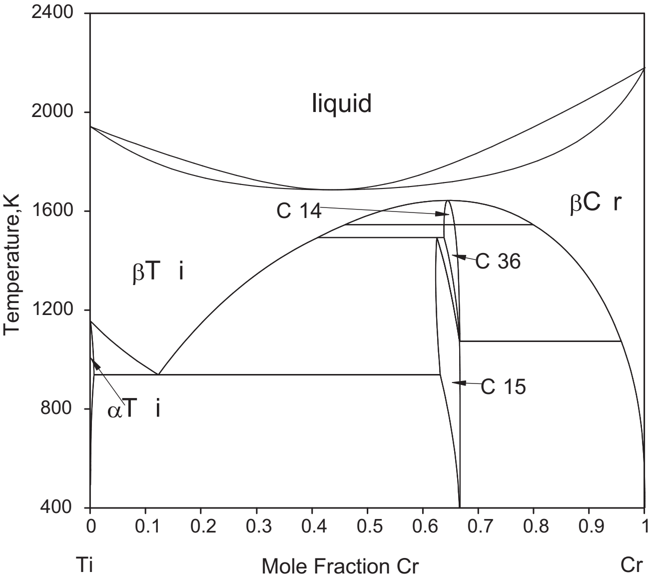

Fig. 2. The Ti–Cr system assessed by Ghosh [21].

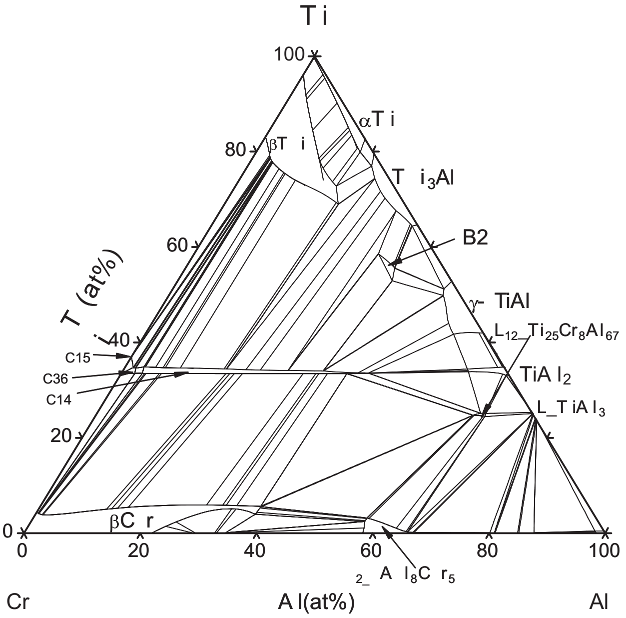

Fig. 4. The calculated isothermal section of the Ti–Al–Cr system at Ti-rich corner at 1073 K.

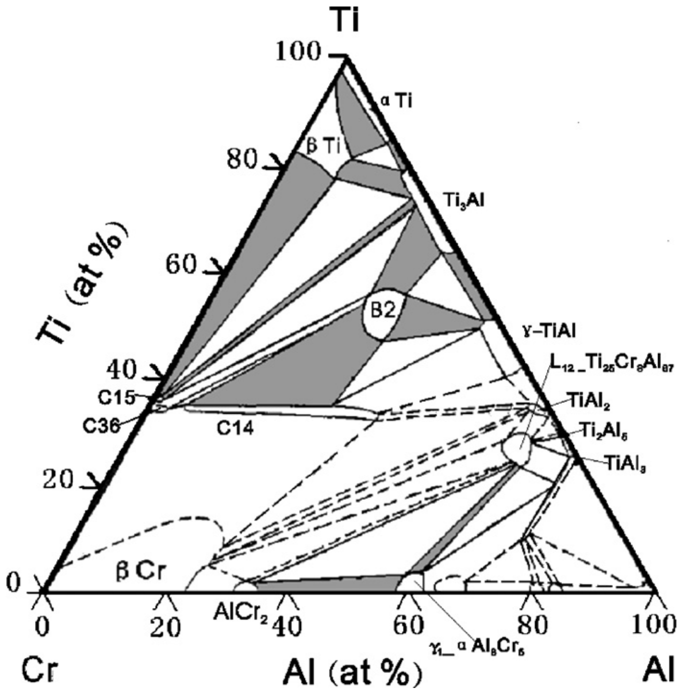

Fig. 5. The experimental phase diagram at 1073 K summarized by Jewett in 1997 [37]. Broken lines are speculative phase boundaries.

the phase equilibria is minimized. This procedure can be conducted as follows: First, the ternary interaction parameters of liquid, bcc, B2 and hcp are calculated; second, the interaction parameters involving the third element in γ-TiAl, Ti_3Al and the Laves phases are optimized. Finally, the thermodynamic parameters of the new ternary compound $L1_2$_$Ti_{25}Cr_8Al_{67}$, the intermetallic compounds $TiAl_2$, $TiAl_3$, Ti_2Al_5, γ_1_βAl_8Cr_5 and γ_2_αAl_8Cr_5 are optimized. All parameters optimized in this work are listed in Table 1.

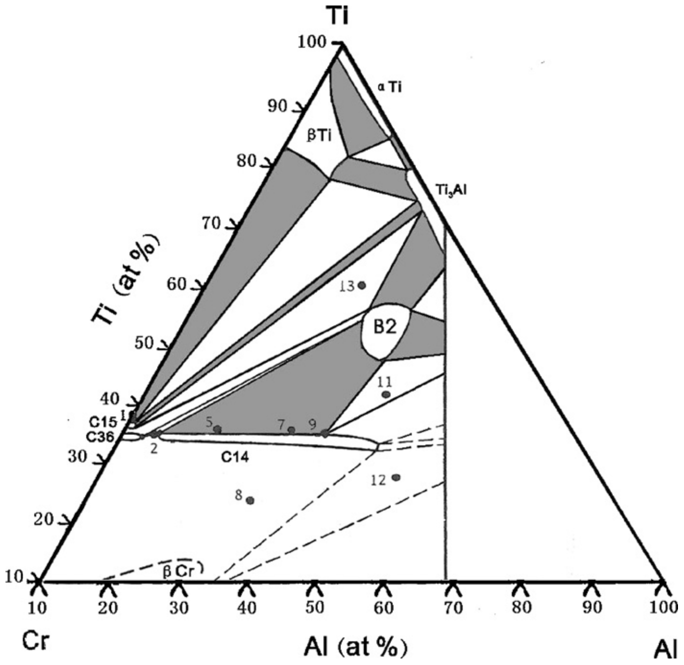

Fig. 6. The experimental phase diagram at 1073 K reported by Jewett et al. in 1996 [40]. Broken lines are speculative phase boundaries.

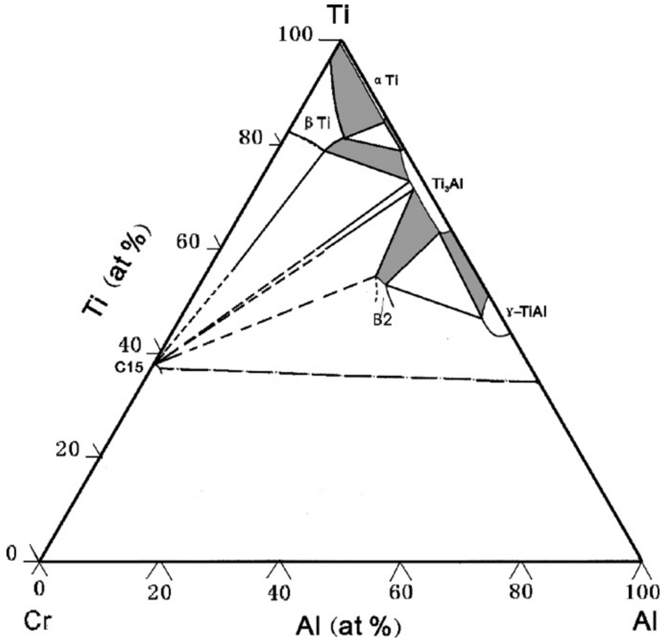

Fig. 7. The experimental phase diagram at 1073 K reported by Ence et al. in 1960s [31]. Broken lines are speculative phase boundaries.

5. Results and discussions

5.1. Binary systems

The Ti–Al phase diagram assessed by Witusiewicz et al. [20], Ti–Cr diagram by Ghosh [21] and Al–Cr diagram by Chen et al. [22] are shown in Figs. 1–3, respectively. The descriptions of these systems are compatible with each other and will be directly utilized for the evaluation of the ternary system Ti–Al–Cr.

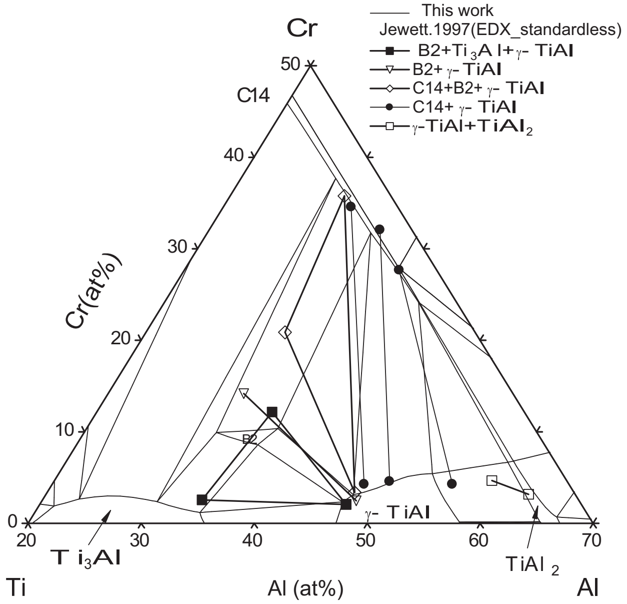

Fig. 8. The calculated isothermal section of the Ti–Al–Cr system at Ti-rich corner at 1073 K along with the experimental data measured by Jewett in 1997 [37].

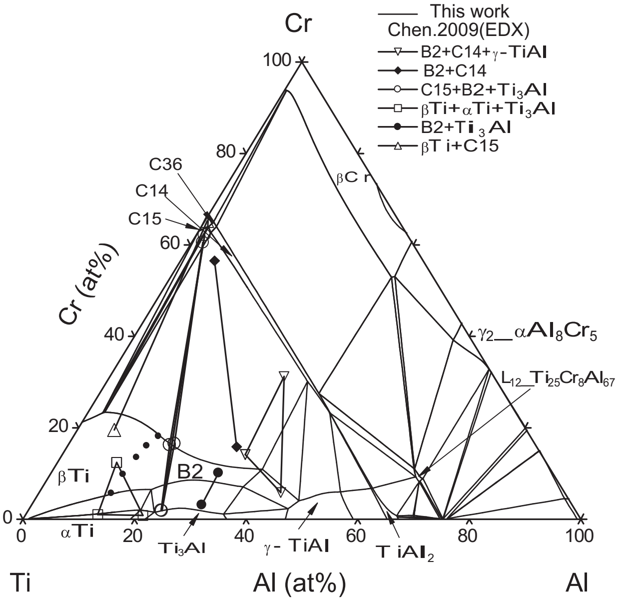

Fig. 9. The calculated isothermal section of the Ti–Al–Cr system at Ti-rich corner at 1173 K along with the experimental data measured by Chen et al. in 2009 [42].

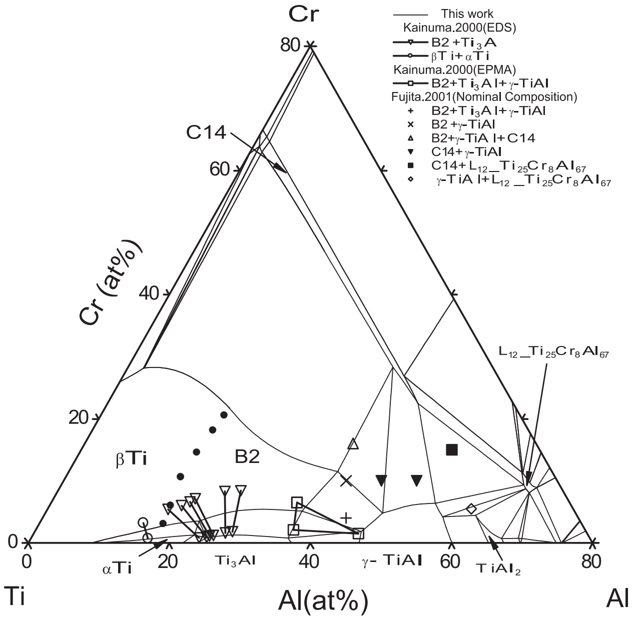

Fig. 11. The calculated isothermal section of the Ti–Al–Cr system at Ti-rich corner at 1273 K along with the experimental data measured by Kainuma et al. [45–46] and Fujita et al. [47].

5.2. Ti–Al–Cr ternary system

5.2.1. Ti-rich corner of Ti–Al–Cr system

Fig. 4 shows the calculated isothermal section at 1073 K, and the related experimental phase diagram summarized by Jewett in 1997 is shown in Fig. 5 [37]. By comparison of Figs. 4 and 5, it can be found that the most of calculated phase equilibria are in good agreement with Jewett's experimental results [37], except that the three phases regions in Fig. 5, B2 + Ti_3Al + C15 and βTi + Ti_3Al + C15, are replaced by B2 + Ti_3Al + C14 and βTi + Ti_3Al + C14 in this work.

This replacement may be reasonable and can be explained as follows: These three phase regions reported by Jewett in 1997 [37] are referred to his earlier works [39–40] and Hayes' results [30], as shown in Figs. 6 and 7, where his interesting is focused on C14, most of the experimental points are centralized in this phase region. His conclusion is that the solubility of the element Al in C14 was about 40 at% at 1073 K and 1273 K, and the Ti content was fixed (about 33 at%) [39–40]. From the Fig. 6 it can be seen that, only the point 13 involves in the three-phase regions of B2 + Ti_3Al + C15 and βTi + Ti_3Al + C15. He also pointed out that due to the small size (<2 μm diameter) of C15 precipitates, the accurate determination of the composition was not possible, which meant that the related phase equilibria cannot be confirmed [40]. Furthermore, his diagrams at 1073K was partially based on the literature reported by Hayes in 1992 [30], which was based on the experimental results reported by Ence et al. in 1960s [31], as shown in Fig. 7. It is obvious that Ence et al. did not confirm the phase equilibrium relationship of the three-phase regions B2 + Ti_3Al + C15 and βTi + Ti_3Al + C15, especially the regions of C15 and B2 phase, which were marked by the

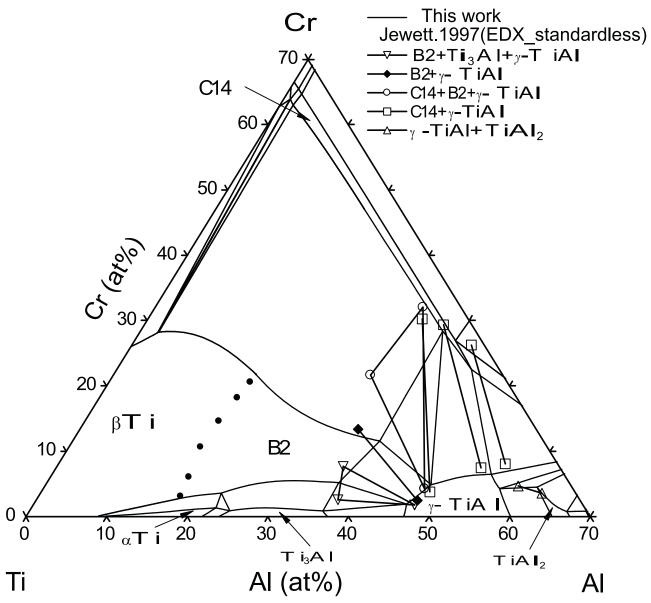

Fig. 10. The calculated isothermal section of the Ti–Al–Cr system at Ti-rich corner at 1273 K along with the experimental data measured by Jewett in 1997 [37].

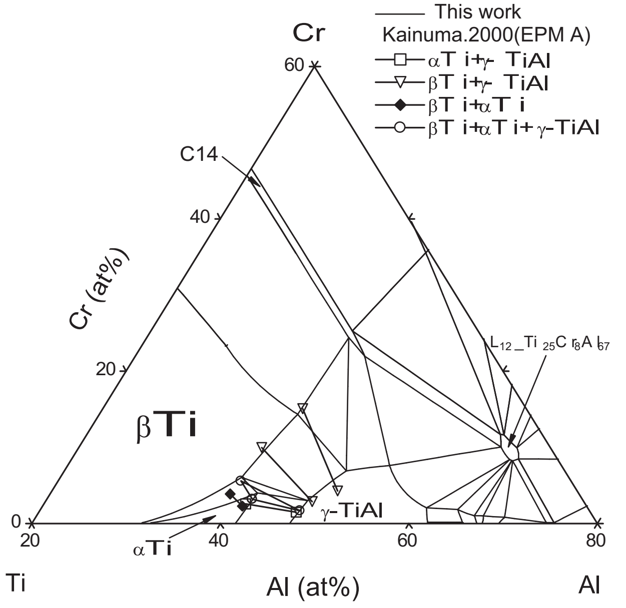

Fig. 12. The calculated isothermal section of the Ti–Al–Cr system at Ti-rich corner at 1473 K along with the experimental data measured by Kainuma et al. [46].

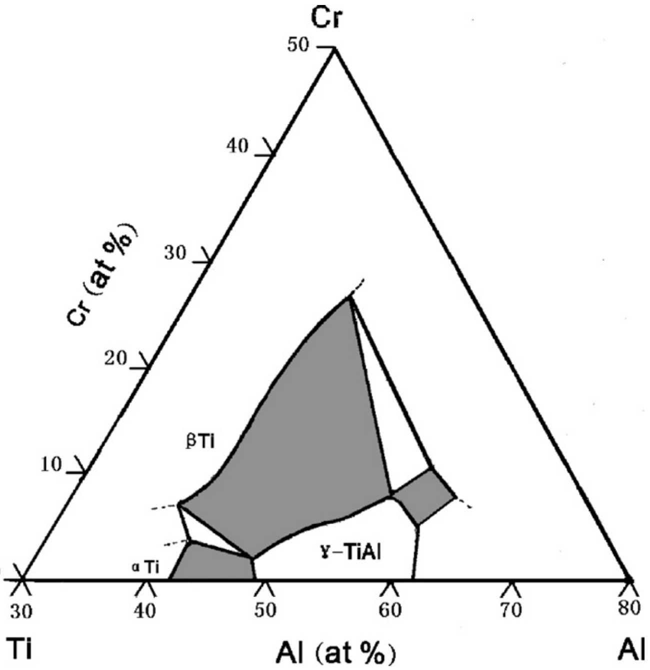

Fig. 13. The experimental phase diagram at 1473 K reported by Fujita et al. [47]. Broken lines are speculative phase boundaries.

broken line. C14 was not presented in Ence et al.'s experimental phase diagram, which was in contradiction to Jewett et al.'s results mentioned-above [39,40]. Therefore, the Ence et al.'s results are not adopted in this work. Besides, the accuracy of measurement for the experimental point 2 in Fig. 6 was doubted by Bochvar et al. [33]. So, we only adopt the conclusion that the solubility of the element Al in C14 was about 40 at% and the Ti content is fixed (about 33 at%) at 1073 K and 1273 K [39,40] and ignored his report about the constitution of three-phase regions. From Fig. 4, it can be seen that the solubility of Al in the C14 calculated in this work are in agreement with Jewett et al.'s result.

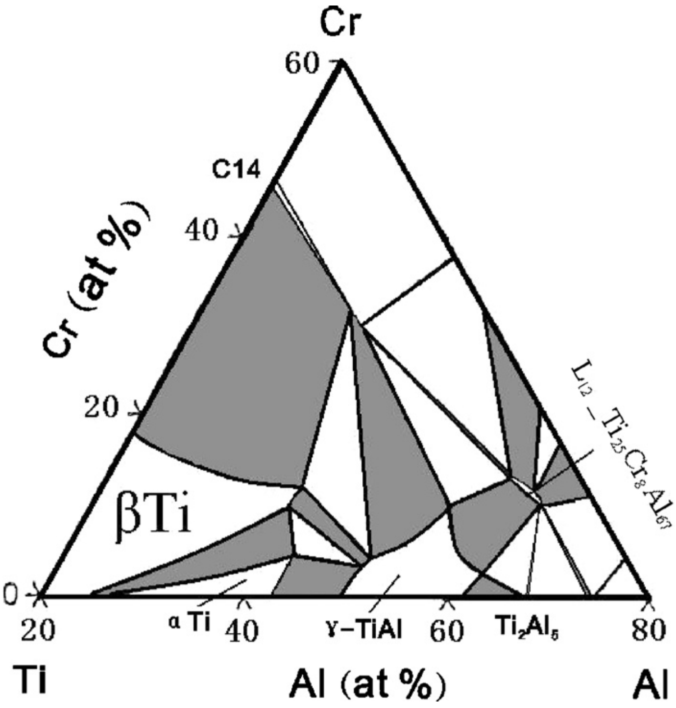

Fig. 14. The experimental phase diagram at 1473 K reported by Hashimoto [48]. Broken lines are speculative phase boundaries.

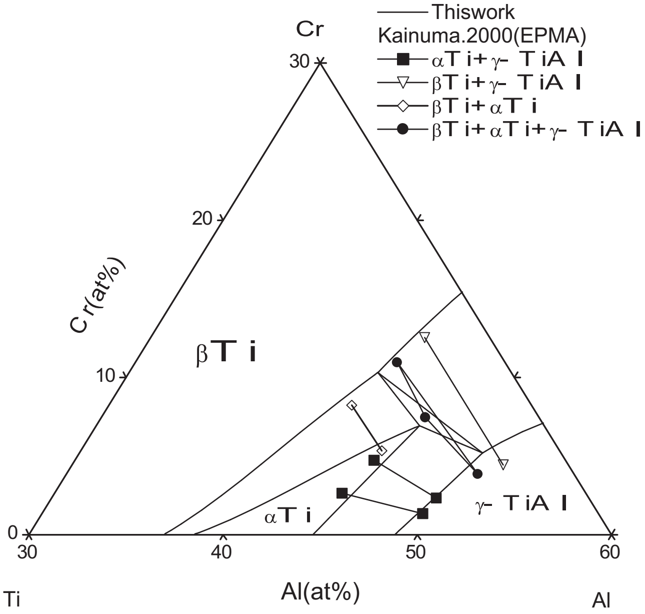

Fig. 15. The calculated isothermal section of the Ti–Al–Cr system at Ti-rich corner at 1573 K along with the experimental data measured by Kainuma et al. [46].

On the basis of his previous' [39,40] and Hayes' [30] experimental results, another study was published by Jewett in 1997 [37]. The related tie-lines and tie-triangles around the γ-TiAl phase were determined by SEM/EDX (stardardless) method [37]. Fig. 8 shows the comparison between the calculated results in this work and the Jewett's results in 1997, from which it can be seen that the calculated results agree well with the most of the experimental results within the error.

Compared with the isothermal section at 1173 K reported by Chen et al. in 2009 [42], it can be seen from Fig. 9 that the calculated results in this work agree well with the most of the experimental results within the error.

Fig. 10 is the calculated isothermal section at Ti-rich corner of the Ti–Al–Cr system at 1273 K and Jewett's experimental results in 1997 [37] is shown in this figure. Fig. 11 shows the calculated isothermal section at 1273 K and the experimental data measured

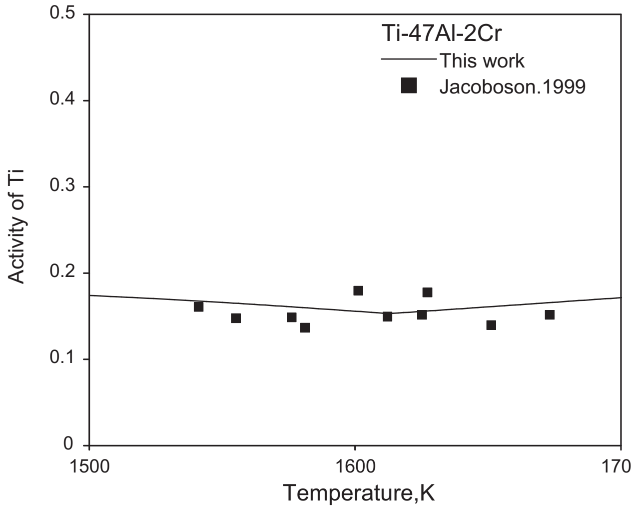

Fig. 16. The calculated activity of Ti in Ti–47Al–2Cr along with the experimental data reported by Jacobson et al. [49]; the reference state is hcp_a3 for Ti.

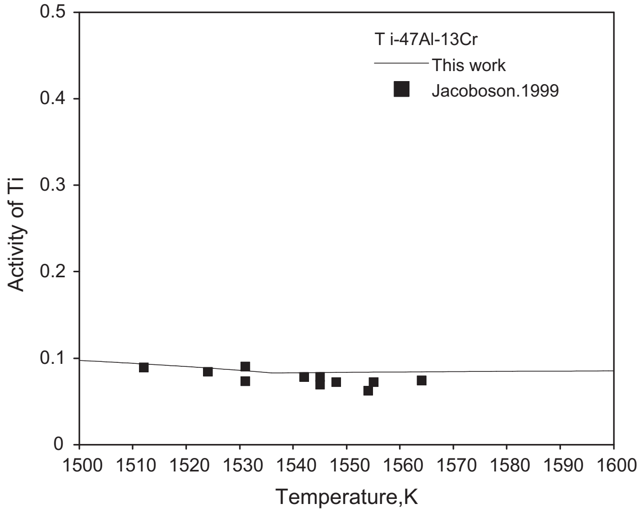

Fig. 17. The calculated activity of Ti in Ti–47Al–13Cr along with the experimental data reported by Jacobson et al. [49]; the reference state is hcp_a3 for Ti.

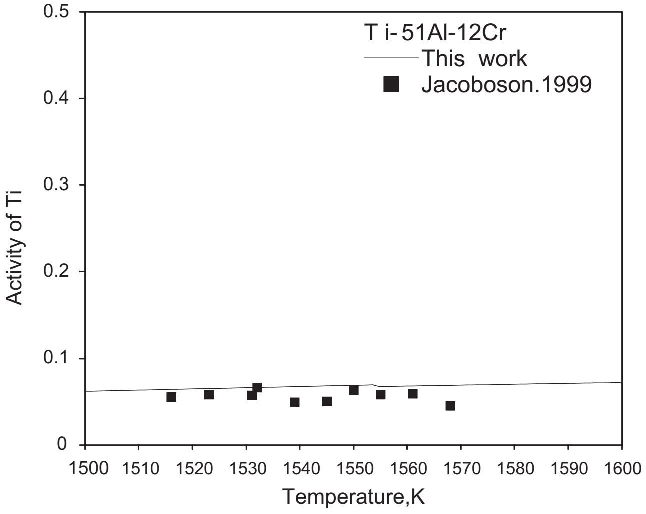

Fig. 18. The calculated activity of Ti in Ti–51Al–12Cr along with the experimental data reported by Jacobson et al. [49]; the reference state is hcp_a3 for Ti.

by Kainuma et al. [45,46] and Fujita et al. [47]. It can be seen that the calculated isothermal at Ti-rich corner at 1273 K are in agreement with the most experimental results within the error.

Fig. 12 shows the calculated section at 1473 K and Kainuma et al.'s experiment results [46]. It can be found that the calculated results are in agreement with the most of experimental results reported by Kainuma. In 2001, Fujita et al. [47] and Hashimoto [48] published the approximate phase equilibrium relationship obtained by XRD method in the same region and most of their results are in good agreements with Kainuma's results near the boundary of Ti-Al. However, there was an argument about whether the C14 existed in this region. Fujita et al. denied this existence but Hashimoto confirmed it, as shown in Figs. 13 and 14.

By observing the trend of activity of the element Ti in the Ti–47Al–13Cr alloy [49], as shown in Fig. 17, a turning point appears at 1540 K, which may imply that the phase transformation of C14 to β(Ti, Cr) will occur at this temperature. Therefore, in this assessment, Hashimoto's experimental results is adopted [48], this imply that C14 exists in 1473 K at Ti-rich corner (30 at% Al–60 at% Al).

Fig. 15 shows the calculated results at 1573 K in this work and Kainuma et al.'s results [46]. It can be seen that the calculated results agree well with the most of the experimental results within the error.

The activities of the element Ti in nominal experimental compositions Ti–47Al–2Cr, Ti–47Al–13Cr and Ti–51Al–12Cr were measured by Jacobson et al. in 1999 [49]. Figs. 16–18 show the comparison between the calculated activities and the experimental ones. It is obvious that the calculated results agree well with the most of the experimental results within the error.

5.2.2. *Al-rich corner of of Ti–Al–Cr system*

The experimental phase equilibrium data at Al-rich corner at 1073 K are not taken into account in this work due to the uncertainties of experiment results, as shown in Fig. 5 [37].

Fig. 19 is the calculated isothermal section at Al-rich corner of the Ti–Al–Cr system at 1273 K compared with Jewett et al.'s experimental results. The experimental data involving $TiAl_3$ is not considered because the solubility of the element Cr in $TiAl_3$ was not determined [41]. It can be found that the calculated results agree well with the most of the experimental results within the error.

Fig. 20 shows the calculated results at 1423 K in this work compared with Park et al.'s [52] and Mabuchi et al's results [53], and the counterpart of experimental phase diagram published by Mabuchi et al. is shown in Fig. 21. Comparing Fig. 20 with Fig. 21, it can be found that most of the calculated phase equilibria are in good agreement with the experimental results within the error. However, the homogeneity range of Ti in C14 calculated in this work is much smaller than the one reported by Mabuchi et al. Mabuchi et al. suggested that the composition of Ti in C14 could be varied from 20 at% to 40 at%, but it is kept around 33 at% in this calculation. This may be explained as follows: the results of C14 reported by Jewett et al. [39,40] and Hashimoto [48] are considered, which assumes that the Ti content in C14 is constant at about 33 at%. Furthermore, the compound $AlCr_2$ is stable at this temperature in the present calculation but it indeed existed in Mabuchi et al.'s experimental phase diagram at 1423 K. This difference may be raised by its extrapolation from the binary Al–Cr system. The latest reported diagram of the Al–Cr system proposes that the $AlCr_2$ is formed by the reaction of $\beta = AlCr_2$ around 1183 K, which is much lower than 1423 K [22]. Therefore, it may be reasonable to consider that this phase is unstable at 1423 K. On the other hand, Mabuchi et al. did not confirm the

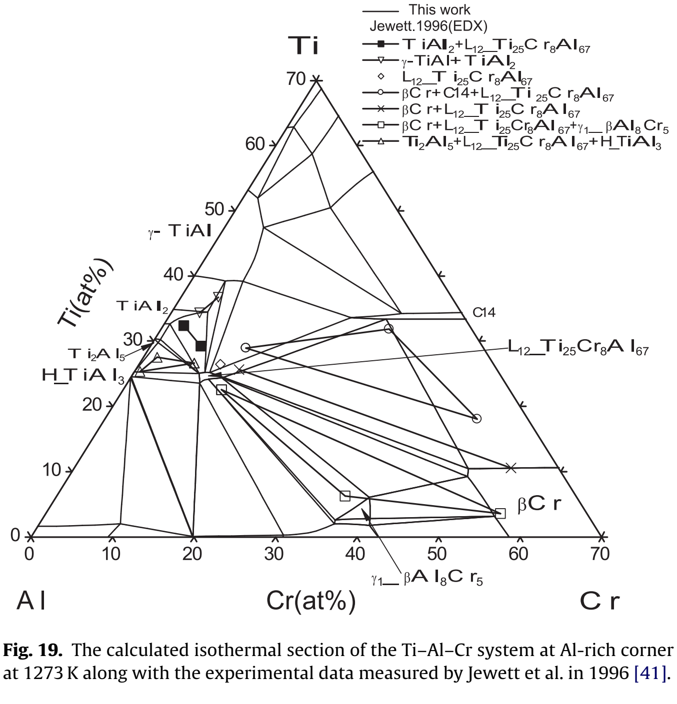

Fig. 19. The calculated isothermal section of the Ti–Al–Cr system at Al-rich corner at 1273 K along with the experimental data measured by Jewett et al. in 1996 [41].

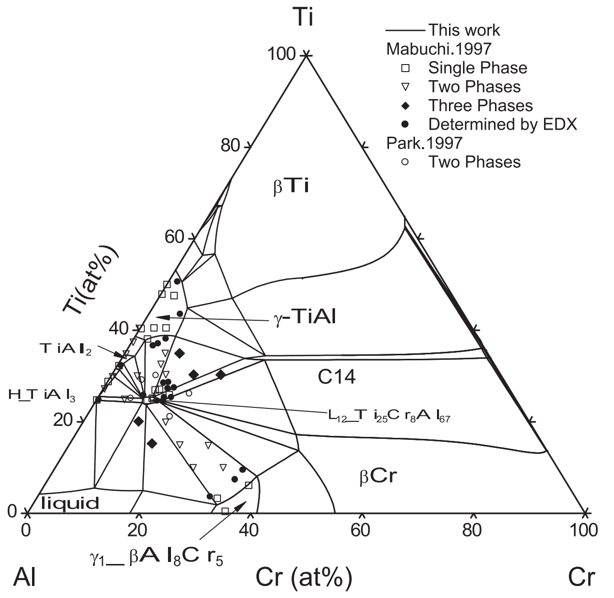

Fig. 20. The calculated isothermal section of the Ti–Al–Cr system at Al-rich corner at 1423 K along with the experimental data measured by Park et al. [52] and Mabuchi et al. [53].

phase equilibrium relationship in these regions, which was marked by a broken line in his experimental phase diagram.

5.2.3. Invariant equilibria

Table 2 lists the temperatures of the invariant reactions with certainty at Ti-rich and Al-rich corners calculated in the present work as well as the values reported by Bochvar et al. [33] and Chen et al. [42], repectively. We also have added liquidus curve projection containing the direction of monovariant lines and their directions for this ternary system, as shown in Fig. 22. It can be seen that the calculated results are in good agreement with the experimental ones.

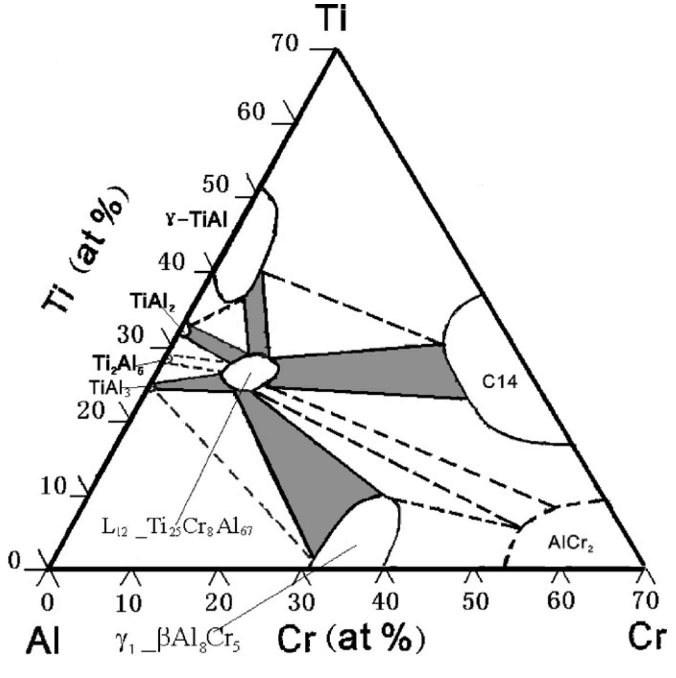

Fig. 21. The experimental phase diagram measured by Mabuchi et al. at 1423 K [53]. Broken lines are speculative phase boundaries.

Table 2
Calculated and experimental results for the invariant reactions in Ti–Al–Cr system.

Reactions	T (K)	Source
At Ti-rich corner		
liquid + αTi = βTi + γ-TiAl(U_1)	1706	[42]
	1623–1763	[33]
	1624	This work
liquid + γ-TiAl = β(Cr,Ti) + $L1_2$_$Ti_{25}Cr_8Al_{67}$(U_2)	1573	[33]
	1583	[42]
	1598	This work
αTi + γ-TiAl = βTi + Ti_3Al	1273–1392	[33]
	~1373	This work
γ-TiAl + $L1_2$_$Ti_{25}Cr_8Al_{67}$ = LavesC14 + $TiAl_2$	1073–1273	[33]
	1173–1273	This work
At Al-rich corner		
liquid + βCr = γ_1_βAl_8Cr_5 + $L1_2$_$Ti_{25}Cr_8Al_{67}$(U_3)	1513	[33]
	1533	[42]
	1524	This work
liquid + Ti_2Al_5 = $L1_2$_$Ti_{25}Cr_8Al_{67}$ + H_$TiAl_3$(U_4)	1603	[33]
	1618	This work
About the formation of $L1_2$_$Ti_{25}Cr_8Al_{67}$		
liquid + γ-TiAl + Ti_2Al_5 = $L1_2$_$Ti_{25}Cr_8Al_{67}$	1623	[33]
liquid + γ-TiAl = $L1_2$_$Ti_{25}Cr_8Al_{67}$ + H_$TiAl_3$	1645	[42]
liquid + γ-TiAl = $L1_2$_$Ti_{25}Cr_8Al_{67}$ + Ti_2Al_5(U_5)	1645	This work

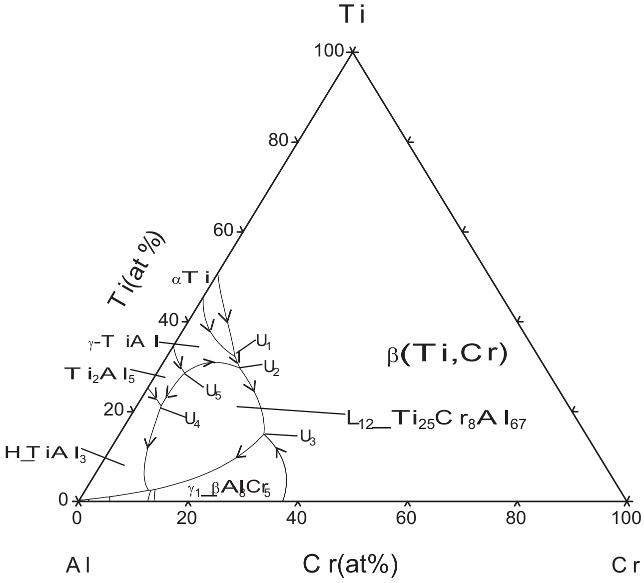

Fig. 22. The calculated liquidus surface projection of the Ti–Al–Cr system.

6. Conclusions

The previous investigations for the Ti–Al–Cr ternary system and the thermodynamic descriptions of the binary systems are reviewed. The model of the ternary Laves phases is taken as $(Al,Cr,Ti)_2(Cr,Ti)$; the model of Ti_3Al is taken as $(Al,Cr,Ti)_3(Al,Ti)$; the model of γ-TiAl is taken as (Al,Cr,Ti) (Al,Cr,Ti); the models of $TiAl_2$, $TiAl_3$ and Ti_2Al_5 are taken as $(Al,Cr,Ti)_m(Al,Ti)_n$; the model of γ_1_βAl_8Cr_5 is taken as $(Al,Cr,Ti)_{17}(Al,Ti)_9$;the model of γ_2_αAl_8Cr_5 is taken as $(Al,Cr,Ti)_{12}(Al,Cr)_5(Al,Cr)_9$ and the model of the new ternary compound $L1_2$_$Ti_{25}Cr_8Al_{67}$ is taken as $(Al,Cr,Ti)_{25}(Al,Cr)_8(Al,Cr,Ti)_{67}$. Based on these models, the Ti–Al–Cr ternary system is assessed by means of the Calphad method using the ternary experimental data in the literature. Then, a series of isothermal sections from 1073 K to 1573 K and some invariant reactions are calculated. It is shown that the present thermodynamic assessment is in good agreement with the majority of experimental results within the error. This assessment may provide the theoretical support to design the low cost titanium alloys related to this system.

Acknowledgements

Thanks are due to Dr. S.L. Chen from CompuTherm LLC, U.S. and Prof. J.Y. Zhang from Shanghai University, China for the helpful discussions in this work. This research is financially supported by Science and Technology Commission of Shanghai Municipality (08DZ2201200 and 10520706400), The National Basic Research Program (973 Program, 2007CB613606), The National Nature Science Foundation of China (NSFC 50774052 and 51074105).

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