AB INITIO AND CALPHAD-TYPE THERMODYNAMIC INVESTIGATION OF THE Ti–Al–Zr SYSTEM

Z.-X. Deng ab, D.-P. Zhao a,*, Y.-Y. Huang b, L.-L. Chen b, H. Zou b, Y. Jiang b, K. Chang b,*

a College of Biology, Hunan University, Changsha, Hunan, China
b Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China

(Received 22 October 2018; accepted 05 September 2019)

Abstract

Ti–Al based alloys have been widely used in the aeronautics and aerospace. Adding alloying element Zr can significantly improve their high-temperature endurance and corrosion resistance. To investigate the influence of the addition of element Zr on the properties of the Ti–Al system, ab initio calculations and the CALPHAD (CALculation of PHAse Diagrams) method were used to evaluate the Ti–Al–Zr ternary system. Ab initio calculations were carried out to calculate the formation enthalpies of intermetallic compounds and end-members. CALPHAD approach was employed to optimize the thermodynamic parameters based on experiments. The experimental data of phase equilibria at 1073, 1273, 1473, and 1573 K, as well as a vertical section of the Ti 3Al–Ti + 5 wt.% Zr were used to assess this system. The thermodynamic parameters of the binary Ti–Al, Al–Zr and Ti–Zr systems were acquired from recent assessments, and the ternary ones were evaluated in the present work. The Ti–Al–Zr ternary dataset has been established and the calculated results are in close agreement with the experimental data on both thermodynamics and phase equilibria.

Keywords: Ti–Al–Zr system; Ab initio calculations; Phase diagrams; Thermodynamic optimization

1. Introduction

Ti–Al based alloys are widely applied in the aeronautics and aerospace, owing to their good high-temperature strength and outstanding oxidation resistance, low density, and low thermal [1-4]. However, the poor room temperature ductility and fracture toughness of Ti–Al alloys significantly limit their applications [5-7]. The addition of elements has been used to improve the mechanical performance of alloy materials for a long time [8-11]. Recently Hashimoto [12] found that the addition of Zr increases the high-temperature endurance and superior corrosion resistance for the Ti–Al base alloys. Furthermore, the addition of Zr also improves ductility and toughness, and thus enhances the processability of Ti–Al base alloys at room temperature [13-15]. The experimental results indicated that Zr could stabilize the highly symmetric cubic ZrAl L1 crystal structure which improves ductility and toughness against the low symmetric tetragonal TiAl D022 structure [15]. The ZrAl phase may serve as a potential nucleation core for α(Al), thus resulting in a homogeneous microstructure with improved machinability of the related Ti–Al alloys [16].

The knowledge of thermodynamics and phase diagrams are constructive in material design, research, and development, especially for the development of the complex alloys [17]. Therefore, the information about phase diagrams of the Ti–Al–Zr system is significant for the design and fabrication of Ti–Al–Zr alloys. So far, there are only a few thermodynamic data and phase diagram data about Ti–Al–Zr system. Ab initio calculations is an effective method to obtain reliable thermodynamic data [18, 19]. The limited experimental data combined with ab initio calculations results are more effective for optimization. After the Ti–Al–Zr dataset is obtained, it can be used as a guidance for the experimental work to significantly reduce costs and resources. Hence, a thermodynamic assessment of the ternary Ti–Al–Zr system is necessary.

2. Literature review

2.1 Ti–Al

There are seven intermetallic compounds in this binary system, i.e., Ti1Al(α2), TiAl(γ), Ti2Al3(η), Ti2Al5(ζ), Ti3Al3(L1), TiAl3(h) and TiAl3(l). Their crystallographic...
data are summarized in Table 1. ‘h’ represents the high-temperature phase and ‘l’ represents the low-temperature phase for TiAl phase. Their Pearson symbol and lattice parameters are different. The researchers [20, 21] assessed the experimental results [22-24], calculated phase diagrams [25-27], and proposed a quite similar phase diagram. Most recently, Witusiewicz et al. [28] reported a thermodynamic description of the Ti–Al system which can reproduce the majority of experimental data on phase equilibria and thermodynamic properties. Therefore, the thermodynamic functions assessed by Witusiewicz et al. [28] were accepted in the present work. The Ti–Al binary phase diagram is shown in Fig. 1 (a).

2.2 Al–Zr

There are ten intermetallic compounds in this binary system, i.e., ZrAl, Zr2Al, Zr3Al, Zr4Al3, Zr5Al4, ZrAl2, ZrAl3, ZrAl4, and ZrAl5. Their crystallographic data are summarized in Table 1. The phase equilibria data before 1992 were reviewed and summarized by Murray [29] and then revised by Okamoto [30] to include the new results of Peruzzi [31]. Batalin et al. [32] determined the activity of Al in Al-rich liquid alloys at 1123 K. Klein et al. [33] determined the standard enthalpy of formation for the ZrAl3 phase from the calorimetric measurement. Meschel and Kleppa [34] measured the standard enthalpies of ZrAl3, and ZrAl4 again by direct synthesis calorimetry at 1473 K. Esin et al. [35] measured the enthalpies of Zr2Al, Zr3Al, and Zr4Al in the temperature range 300 to 2000 K. Wang et al. [36] optimized the Al–Zr binary system combined with previous work, and the results are in good agreement with the experimental data [31, 37, 38]. Therefore, the optimized parameters done by Wang et al. [36] are adopted. The Al–Zr binary phase diagram is shown in Fig. 1 (b).

2.3 Ti–Zr

There are no intermetallic compounds in this binary system. The phase relationship of the Ti–Zr system are relatively simple. There are only three stable solution phases in this system, i.e., the liquid, bcc, and hcp phase. It is characterized by two congruent transformations: liquid to bcc, and bcc to hcp. The system was critically evaluated by Murray [44, 45], and then it was optimized based on the available experimental data [46, 47] by Hari Kumar et al. [48]. The results show a good agreement with experimental data [46, 47]. The thermodynamic description of the Ti–Zr system reported by Hari Kumar et al. [48] is chosen in the present work. The Ti–Zr binary phase diagram is shown in Fig. 1 (c).

2.4 Ti–Al–Zr

Shirokova et al. [49] determined the TiAl–Ti + 5 wt.% Zr vertical section of the Ti–Al–Zr system with Equilibrated Alloys (EA) and Microanalysis (MA) methods. Numerous samples with different compositions were prepared and annealed at 1073 K for 1100 hours. The microstructure of each alloy was obtained by MA, followed by the Thermal Analysis (TA) to determine the phase boundary of α, α′, Ti3Al, b, and liquid phases. Kainuma et al. [50] measured the phase equilibria in the Ti-rich corner of the Ti–Al–Zr system at 1273, 1473, and 1573 K by Electron Probe Micro Analysis (EPMA). Yang et al. [51] investigated the phase equilibria at 1273 K through alloy sampling combined with EPMA and XRD. The BSE images and XRD results intuitively reflected the phase regions. The composition of each phase was obtained by EPMA (Standard deviations of the measured concentration is ± 0.6 at.%), and thus the phase boundary was determined. The works of Yang et al. [51] were assessed to be more reliable than others [52, 53] due to the intuitive and accurate experimental results, higher emphasis would be placed on these data [51] in the present optimization. More recently, Lü et al. [52] determined the phase relationships at 1073 K (temperature error is within ± 5 °C) using equilibrated alloys and diffusion couple approach. They declared that there were two three-phase regions of TiAl + Ti3Al + b(Ti, Zr) and TiAl + ZrAl2 + b(Ti, Zr) in the diffusion couple. However, there were no obvious contrasts in the BSE images and no XRD patterns were presented for equilibrated alloys or diffusion couples. The two three-phase regions [52] remained uncertain and thus were not considered in the present work. Instead, we used other phase equilibria data [52] with solid evidences in the optimization. Ghosh et al. [53] calculated the enthalpies of formation along the TiAl3–ZrAl3 section. They only calculated five different points and there was no experimental data to support their results [53]. Therefore, we did not accept their data [53] in the present work. According to the reported data [50-53], no ternary compound exist in the ternary system. Table 2 summarizes the experimental data of the Ti–Al–Zr system accepted in the present optimization.

3. Methods and models

3.1 Ab initio calculations

The ab initio calculations based on density functional theory were carried out using the Vienna ab initio simulation package (VASP) [55], wherein projector augmented plane-wave potentials were employed [56]. The generalized gradient approximation (GGA) method was performed with the Blöchl corrections for the total energy [57]. A
plane-wave cutoff energy of 550 eV and an energy convergence criterion of 0.01 meV for electronic structure self-consistency were used. The integration in the Brillouin zone was performed on appropriate k-points, which was determined according to the Monkhorst-Pack method [58]. All structures are relaxed with respect to atomic positions and volumes.

In the present work, the formation enthalpy, $\Delta H_f (Me_{x}Al_{y}, Me=Ti \text{ or } Zr)$ at 0 K is expressed by the following equation:

$$\Delta H_f (Me_{x}Al_{y}) = E(Me_{x}Al_{y}) - \left[ x_{Me}E(Me) + x_{Al}E(Al) \right]$$

Where $E(Me_{x}Al_{y})$, denote the total energy of $Me_{x}Al_{y}$, $E(\text{Me})$ and $E(\text{Al})$ are the energies of pure element for particular reference state.

$\alpha Me$ (Me = Ti or Zr) is the atomic fraction of the component.

### 3.2 CALPHAD

The CALPHAD-type modeling was performed with the step-by-step optimization procedure described by Du et al. [59]. The reliable experimental data and the enthalpies of formation for the compounds via $ab$ intitio calculations were employed.

| Phase          | Space Group | Pearson symbol | Proto–type | Lattice parameters (Å) | References |
|----------------|-------------|----------------|------------|------------------------|------------|
| $\alpha(Al)$   | $Fm\bar{3}m$ | cF4            | Cu         | a 4.049 ; b 4.049 ; c 4.049 | Al-5 vol.% Al3Zr [39] |
| $\alpha(Ti)$   | $P63/mmc$   | hP2            | Mg         | 2.95 ; 2.95 ; 4.684    | Pure $\alpha Ti$ [40] |
| $\alpha(Zr)$   | $P63/mmc$   | hP2            | Mg         | 3.232 ; 3.232 ; 3.148   | Pure $\alpha Zr$ [40] |
| $\beta(Ti)$    | $Im\bar{3}m$| cI2            | W          | 3.307 ; 3.307 ; 3.307   | Pure $\beta Ti$ [41] |
| $\beta(Zr)$    | $Im\bar{3}m$| cI2            | W          | 3.609 ; 3.609 ; 3.609   | Pure $\beta Zr$ [41] |
| $\text{Ti}_3\text{Al}\alpha(2)$ | $P63/mmc$   | hP8            | Ni3Sn      | 5.806 ; 5.806 ; 4.655   | [42] |
| $\text{TiAl}(\gamma)$ | $P4/\overline{mmn}$ | tP4          | CuAu       | 2.829 ; 2.829 ; 4.071   | This work (cal.) |
| $\text{Ti}_3\text{Al}_\alpha$ | $P4/\overline{mnb}$ | tP32         | Ti$_3$Al$_\alpha$ | 11.293 ; 11.293 ; 4.038  | This work (cal.) |
| $\text{TiAl}(\alpha)$ | $I41/amd$   | tI24           | HfGa$_2$   | 3.97 ; 3.97 ; 24.309    | [24] |
| $\text{TiAl}({\tilde{C}})$ | $P4/\overline{mmn}$ | tP28         | Ti$_3$Al$_\alpha$ | 3.905 ; 3.905 ; 29.196  | This work (cal.) |
| $\text{TiAl}(\beta)$ | $I4/\overline{mmn}$ | tI8            | TiAl$_\beta$ | 3.863 ; 3.863 ; 8.648   | This work (cal.) |
| $\text{TiAl}(\iota)$ | $I4/\overline{mmn}$ | tI32           | TiAl$_\beta$ | 3.987 ; 3.875 ; 33.84   | This work (cal.) |
| $\text{Zr}_3\text{Al}$ | $Pm\bar{3}m$ | cP4            | Cu$_3$Au   | 4.373 ; 4.373 ; 4.373   | [21] |
| $\text{Zr}_3\text{Al}$ | $P63/mmc$   | hP6            | Ni$_3$In   | 4.882 ; 4.882 ; 5.918   | This work (cal.) |
| $\text{Zr}_3\text{Al}_\alpha$ | $I4/mcm$   | tI32           | W$_3$Si$_3$ | 11.042 ; 11.042 ; 5.393  | This work (cal.) |
| $\text{Zr}_3\text{Al}_2$ | $P42/\overline{mmm}$ | tP20         | Zr$_3$Al$_2$ | 7.632 ; 7.632 ; 6.997   | [29] |
| $\text{Zr}_3\text{Al}_3$ | $P6/\overline{mmm}$ | hP7            | Zr$_3$Al$_3$ | 5.43 ; 5.43 ; 5.39    | [29] |
| $\text{Zr}_5\text{Al}_4$ | $P63/mcm$   | hP18           | Ga$_4$Ti$_3$ | 8.447 ; 8.447 ; 5.785   | [29] |
| $\text{ZrAl}$   | $\text{Cmcm}$ | oC8            | CrB        | 3.36 ; 10.89 ; 4.27     | [29] |
| $\text{Zr}_3\text{Al}_4$ | $Fd\bar{d}2$ | of40          | Zr$_3$Al$_4$ | 9.601 ; 13.91 ; 5.578   | This work (cal.) |
| $\text{Zr}_3\text{Al}_4$ | $P63/mmc$   | hP12           | MgZn$_2$  | 5.28 ; 5.28 ; 8.748   | This work (cal.) |
| $\text{Zr}_5\text{Al}_4$ | $I4/mmm$   | tI16           | Zr$_5$Al$_4$ | 4.01 ; 4.01 ; 17.3   | [29] |

Table 1: List of symbols and crystallographic data of the phases in the Ti–Al–Zr system
as input data. The evaluation of the thermodynamic parameters was performed by the optimization program PARROT [60] of the Thermo-Calc software, which works by minimizing the square sum of the differences between measured and calculated values. Thermodynamic models used in the CALPHAD-type modeling are listed as follows.

3.2.1 Unary phases

The Gibbs energy function $G_i^o(T) = G_i^0(T) - H_i^{SER}$ for element $i$ (Ti, Al, Zr) in the phase $\varphi$ (liquid, bcc_A2, hcp_A3 and fcc_A1) is expressed by the following equation:

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

Where $H_i^{SER}$ is the molar enthalpy of the element $i$ at 298.15K and 1 bar in its standard element reference (SER) state, and $T$ is the absolute temperature. In the present modeling, the Gibbs energies for pure elements (Ti, Al, Zr) were taken from the compilation by Dinsdale [61].

3.2.2 Solution phases

The Gibbs energies of solution phase $j$ are expressed by the following equation:

$$G_{j}^o - H_j^{SER} = \sum_{i=1}^{k} x_i G_{i}^0 + RT \sum_{i=1}^{k} x_i \ln(x_i) + \sum_{i=1}^{k} G_{i}^{SER}$$

in which $H_j^{SER}$ is the abbreviation of $x_{Ti}H_{Ti}^{SER} + x_{Al}H_{Al}^{SER} + x_{Zr}H_{Zr}^{SER}$, $x_i$ is the molar fractions of component

Table 2. Summary of the phase equilibria and thermodynamic data in the Ti–Al–Zr system

| Reference        | Type of data                      | Method       |
|------------------|-----------------------------------|--------------|
| Shirokova et al. [49] | Vertical section of the Ti3Al to Ti+5%Zr(mass fraction) | EA, MA & TA  |
| Kainuma et al. [50] | Partial isothermal sections at 1273, 1473 and 1573K in the Ti-rich corner | EA & EPMA   |
| Premkumar et al. [54] | Phase relationships of aTi, bTi and g(TiAl) at 1473K | EA, XRD & TEM |
| Yang et al. [51] | Isothermal sections at 1273K | EA, XRD & EPMA |
| Lü et al. [52] | Isothermal sections at 1073K | DC, EA & EPMA |

Figure 1. The calculated phase diagram of (a) Ti–Al [28], (b) Al–Zr [36] and (c) Ti–Zr [48] binary systems

Table 2. Summary of the phase equilibria and thermodynamic data in the Ti–Al–Zr system

DC = Diffusion couples; EA = Equilibrated alloys; EPMA = Electron probe microanalysis; XRD = X-ray diffraction; TEM = Transmission electron microscopy; MA = Microanalysis; TA = Thermal Analysis


\[ G^\text{zr al} = y_{\text{zr}} G^\text{zr} + y_{\text{al}} G^\text{al} + y_{\text{ti}} G^\text{ti} + \frac{1}{2} y_{\text{zr}} y_{\text{al}} G^\text{zr al} + \frac{1}{2} y_{\text{zr}} y_{\text{ti}} G^\text{zr ti} + \frac{1}{2} y_{\text{al}} y_{\text{ti}} G^\text{al ti} + \frac{1}{2} y_{\text{zr}} y_{\text{al}} y_{\text{ti}} G^\text{zr al ti} \]

\[ xRT(y_{\text{zr}} \ln y_{\text{zr}} + y_{\text{al}} \ln y_{\text{al}} + y_{\text{ti}} \ln y_{\text{ti}}) \]

\[ A + B \cdot T + x_{\text{zr}} G_{\text{zr}} + x_{\text{al}} G_{\text{al}} + x_{\text{ti}} G_{\text{ti}} \]

\[ L_{\text{zr al}} = x_{\text{zr}} L_{\text{zr}} + x_{\text{al}} L_{\text{al}} + x_{\text{ti}} L_{\text{ti}} \]

Where \( L_{ij} \) denote the number of sites in each sublattice, \( y_{\text{zr}}, y_{\text{al}}, y_{\text{ti}}, y_{\text{zr al}}, y_{\text{zr ti}}, y_{\text{al ti}}, y_{\text{al zr}}, y_{\text{al ti}}, y_{\text{zr ti}}, y_{\text{zr al ti}} \) represent the site fractions of Zr, Al, Ti, Zr-Al, Zr-Ti, Al-Ti, Al-Zr, Ti-Zr, Ti-Al, Al-Zr respectively.

**3.2.3 Intermetallic compounds**

In the present work, the intermetallic compounds in the Ti–Al–Zr system are divided into three types. The first type, such as the ZrAl and Zr2Al3 phases, is modeled as stoichiometric compounds. The Gibbs energy of each phase is given by the following expression:

\[ G^\varphi = x_{\text{zr}} G_{\text{zr}} + x_{\text{al}} G_{\text{al}} + x_{\text{ti}} G_{\text{ti}} + \frac{1}{2} x_{\text{zr}} x_{\text{al}} G_{\text{zr al}} + \frac{1}{2} x_{\text{zr}} x_{\text{ti}} G_{\text{zr ti}} + \frac{1}{2} x_{\text{al}} x_{\text{ti}} G_{\text{al ti}} + \frac{1}{2} x_{\text{zr}} x_{\text{al}} x_{\text{ti}} G_{\text{zr al ti}} \]

\[ xRT(y_{\text{zr}} \ln y_{\text{zr}} + y_{\text{al}} \ln y_{\text{al}} + y_{\text{ti}} \ln y_{\text{ti}}) \]

The calculated formation enthalpies of the intermetallic compounds of the Ti–Al and Al–Zr system are summarized and shown in Table 2 and Fig. 2. Fig. 2 (a) shows the lattice parameters of Ti–Al compounds that were calculated by \textit{ab initio} along with literature data [24, 42, 43]. Fig. 2 (b) shows the Al–Zr compounds along with literature data [21, 29]. The calculated results fit very well with literature data, with a deviation of 0.35–1.46%.

The calculated formation enthalpies of the intermetallic compounds of the Ti–Al and Al–Zr system are summarized and shown in Table 4 and Fig. 3. Fig. 3 (a) shows the formation enthalpies of Ti–Al system with reference data [63–66], showing a good agreement. Fig. 3 (b) presents the comparison between the formation enthalpies of Al–Zr system and the data available in the literature [33, 34, 36, 38, 67, 68]. The calculated results have a good agreement with literature data except Wang et al. [36]. The results from Wang et al. [36] are obtained by calculation, and the results of other researchers are gained through experiments. Therefore, our results are reliable.
Table 3. Summary of the thermodynamic parameters in the Ti–Al–Zr system by the present work. DC = Diffusion couples; EA = Equilibrated alloys; EPMA = Electron probe microanalysis; XRD = X-ray diffraction; TEM = Transmission electron microscopy; MA = Microanalysis.; TA = Thermal Analysis.

| Phase | Models | Parameters |
|-------|--------|------------|
| Liquid (Al, Ti, Zr) | $L_{Al,Ti,Zr}^{Liquid} = -200000$ | |
| HCP (Al, Ti, Zr) | $L_{Al,Ti,Zr}^{HCP} = -32190 \text{ to } -307^\circ$ | |
| BCC (Al, Ti, Zr) | $L_{Al,Ti,Zr}^{BCC} = -107300 \text{ to } -1007^\circ$ | |
| BCC (Al, Ti, Zr) | $L_{Al,Ti,Zr}^{BCC} = -50000$ | |

4.2 Vertical section

Fig. 4 shows the calculated vertical section of the TiAl–Ti + 5 wt.% Zr by PANDAT [69] software, and the experimental data from Shirokova et al. [49]. It can be seen that the calculation results are in good agreement with the experimental values.

4.3 Isothermal section

Fig. 5 (a)–(c) shows the calculated isothermal sections of the Ti-rich corner of the Ti–Al–Zr system at 1273, 1473, and 1573 K, respectively. The experimental points [50] are marked as a black circle. At 1273 and 1473 K, compared to the experimental data, the optimization results are not very good. Especially for a(hcp_A3) phase, not all the experimental points are on the phase boundary. When the a(hcp_A3) phase parameters of the Ti–Al binary system [28] are adjusted, this can be avoided. It may
Figure 2. Variation of lattice parameters of (a) Ti–Al binary system along with references [24, 42, 43] and (b) Zr–Al binary system along with references [21, 29]

Figure 3. The enthalpy of formation of (a) Ti–Al binary system (reference state is hcp Ti and fcc Al) along with the experimental data [63-66] and (b) Zr–Al binary system (reference state is hcp Zr and fcc Al) along with the experimental data [33, 34, 36, 38, 67, 68]

| Compounds | Kubaschewski [63] | Stuve [64] | Meschel [65] | Nassik [66] | This work (cal.) |
|-----------|-------------------|------------|--------------|-------------|-----------------|
| Ti₃Al     |                   |            |              |             | -27.01          |
| TiAl      | -40.1             |            |              | -35.1       | -39.3           |
| Ti₃Al₂    | -40.9             | -36.9      | -36.6        | -47         | -38.39          |

Table 4. Summary of formation enthalpies of the Ti-Al intermetallic compounds, kJ/(mole of atoms)

| Compounds | Kematiek [38] | Alcock [67] | Meschel [34] | Klein [33] | Saunders [68] | Wang [36] | This work (cal.) |
|-----------|---------------|-------------|--------------|------------|----------------|----------|-----------------|
| Zr₂Al     |               | -27         | -36.2        | -29.2      |                |          |                 |
| Zr₃Al     | -48           | -33.4       | -48.4        | -34.9      |                |          |                 |
| Zr₃Al₂    | -49           | -36.2       | -51.5        | -36        |                |          |                 |
| Zr₅Al₃    | -52           | -58.5       | -44.4        | -44.4      |                |          |                 |
| Zr₅Al₄    | -53           | -44.5       | -65          | -45.3      |                |          |                 |
| Zr₆Al₃    | -55           | -46.9       | -56.6        | -50.4      |                |          |                 |
| Zr₆Al₄    | -54           | -46.9       | -56.6        | -50.4      |                |          |                 |
| Zr₆Al₅    | -49           | -46.9       | -56.6        | -50.4      |                |          |                 |
result from the error of the parameters [28] at the a(hcp_A3) phase in Ti-Al binary system. Generally, the phase relationships are correct, and the optimization results are acceptable. At 1573 K, the a(Ti,Al) phase and the g(TiAl) phase are in good agreement with the experimental data.

Fig. 6 (a) is the calculated isothermal section of the Ti–Al–Zr system at 1073 K. There are 15 three-phase regions inside. Eight of them have been proved to exist by Lü et al [52]. Six of them are concluded by experiments. The remaining one phase appears in the present work. For the eight three-phase regions which have been proved to exist by experiment [52], e(TiAl, h) + η(TiAl) + ZrAl, η(TiAl) + ZrAl, g(TiAl), ZrAl, ZrAl, η(TiAl) + ZrAl, η(TiAl) + ZrAl, and ZrAl + b(Ti, Zr) are obtained by equilibrated alloys. But the ZrAl + ZrAl + ZrAl, ZrAl + ZrAl + b(Ti, Zr) are not in good agreement with experimental points. Considering the measuring error in experiments, this small difference between the calculated phase diagram and the experimental data can be acceptable. Other three three-phase regions fit well with experimental data. a(Ti) + a(TiAl) + b(Ti, Zr), a(Ti,Al) + b(Ti, Zr) + g(TiAl) and b(Ti, Zr) + g(TiAl) + ZrAl three-phase regions are gained by diffusion couple. Two three-phase regions of TiAl + TiAl + b(Ti, Zr) and TiAl + ZrAl + b(Ti, Zr) were proposed by Lü et al [52], while our calculations show phase equilibria of TiAl + TiAl + ZrAl, and TiAl + ZrAl + ZrAl, at 1073 K. However, direct experimental proof of the two three-phase regions is not presented in Lü et al [52], and further experiments are needed. It is also found that introduction of ternary parameters cannot alter the phase relationship to fit the results in Lü et al [52]. Adjusting the binary parameters can be carried out but only based on future solid experimental evidence. The other six three-phase regions, liquid + e(TiAl, h) + ZrAl, ZrAl, ZrAl + ZrAl, ZrAl, ZrAl, a(TiAl) + b(Ti, Zr), ZrAl + ZrAl + b(Ti, Zr), ZrAl + ZrAl + b(Ti, Zr) and ZrAl + b(Ti, Zr) + a(Zr), are reasonably inferred by the experiment. It appears in the present work. But one of them is different from the experiments. a(TiAl) + ZrAl + b(Ti, Zr), appears in the optimized isothermal section while ZrAl + ZrAl + b(Ti, Zr) appears in the experimental phase diagram. There is one new three-phase region in this isothermal section compared with the experimental data, and the region is e(TiAl, h) + e(TiAl, l) + TiAl. In the binary phase diagram of Ti–Al at 1073 K [28], the e(TiAl) existed both at high and low temperature, so the existence of this region is reasonable. Over the whole composition range, the result is acceptable.

Fig. 6 (b) is the calculated isothermal section of the Ti–Al–Zr system at 1273 K. This isothermal section includes 14 three-phase regions. Among them, ten three-phase regions have been completely determined by Yang et al. [51], e(TiAl, h) + ζ(Ti2Al5) + ZrAl, ζ(Ti2Al5) + ZrAl + η(TiAl), η(TiAl) + ZrAl + η(TiAl), η(TiAl) + ZrAl + g(TiAl), g(TiAl) + ZrAl + ζ(Ti2Al5), ZrAl + ZrAl + ZrAl, ZrAl + ZrAl + ζ(Ti2Al5), ZrAl + g(TiAl) + ZrAl + ZrAl + ZrAl, a(TiAl) + b(Ti, Zr) + b(Ti, Zr) and ZrAl + ZrAl + b(Ti, Zr), which are represented by red areas. Nine three-phase regions are in good agreement with experimental points, except ZrAl + ZrAl + ZrAl. The alloy composition prepared by Yang et al. [51] is out of the ZrAl + ZrAl + ZrAl three-phase region. It was found that the phase equilibrium is strongly affected by the negative Gibbs energy of the ZrAl phase at 1273 K, one can only adjust the thermodynamic parameters of this phase to fit the experimental data. However, it is beyond the scope of the present work to modify the binary system based on one single ternary experimental point. Therefore, instead of the alloy composition data, only the phase relationship ZrAl + ZrAl + ZrAl was considered in the optimization. The remaining four three-phase regions, liquid + e(TiAl, h) + ZrAl, ZrAl, ZrAl, ZrAl + ZrAl, ZrAl, ZrAl, ZrAl, ZrAl, and b(Ti, Zr) + a(TiAl) + ZrAl, are reasonably inferred by experiment, which are represented by green areas in the figure.

Figure 4. Selected isopleth in the Ti–Al–Zr system showing calculated equilibria (lines). Experimental data [49] are shown as symbols.
5. Conclusions

The Ti–Al–Zr system has been thermodynamically investigated with the three sub-binary systems and ternary experimental phase diagram data using ab initio calculations and the CALPHAD method. The Ti–Al–Zr ternary dataset is established. The results can be summarized as follows:

1. The lattice parameters and the total energy of related phases are calculated by ab initio, and the results are in good accordance with the experimental data.
2. The calculated isothermal section of the Ti–Al–Zr system at 1273 K is in close agreement with the experimental data. For the isothermal section at 1073 K, the three-phase regions of TiAl + Ti₃Al + b(Ti, Zr) and TiAl + ZrAl₂ + b(Ti, Zr) cannot be reproduced and more experimental data are needed. The results of the

Figure 5. Phase boundary of the Ti-rich corner of the Ti–Al–Zr ternary system at (a) 1273 K, (b) 1473 K and (c) 1573 K, along with experimental data

Figure 6. Calculated isothermal section of Ti–Al–Zr system at (a) 1073 K, compared with the experimental data [51] and (b) 1273 K, compared with the experimental data [52]
Ti-rich corner of the Ti–Al–Zr system at 1273, 1473, and 1573 K are consistent with the experimental values as well. The TiAl–Ti + 5 wt.% Zr vertical section of the Ti–Al–Zr system is in good agreement with experiments.

3. One new three-phase region at 1073 K has been predicted by the calculation, i.e., \( e(\text{TiAl}_3) + e(\text{TiAl}_2) + \text{TiAl} \). The existence of this region is reasonable through our analysis compared with the experimental data.

Acknowledgement

Financial support from National Natural Science Foundation of China (51604104 and 51701232) and CAS Pioneer Hundred Talents Program is acknowledged.

References

[1] E. Bayraktar, Int. J. Fatigue, 26 (2004) 1263-1275.
[2] T.G. Nieh, L.M. Hsiung, J. Wadsworth, Intermetallics, 7 (1997) 163-170.
[3] Y. Wang, Y. Liu, G. Yang, H. Li, B. Tang, Trans. Nonferrous Met. Soc. China, 21 (2011) 215-222.
[4] W. Chen, Y. Guan, Z. Wang, Trans. Nonferrous Met. Soc. China, 26 (2016) 369-377.
[5] C.T. Liu, J.L. Wright, S.C. Deevi, Mater. Sci. Eng., A, 329-331 (2002) 416-423.
[6] Y. Jin, J.N. Wang, J. Yang, Y. Wang, Scr. Mater., 51 (2004) 1263-1275.
[7] G. Hénaff, A.-L. Gloanec, Intermetallics, 13 (2005) 543-558.
[8] A. Luo, M. Pekguleryuz, J. Mater. Sci., 29 (1994) 5259-5271.
[9] B. Argent, J. Crangle, J. Less-Common Met., 109 (1985) 375-380.
[10] Y. Ke, H. Duan, Y. Sun, Mater. Sci. Eng., A, 528 (2010) 220-225.
[11] G.S. Fox-Rabinovich, D.S. Wilkinson, S.C. Veldhuis, G.K. Dosbaeva, G.C. Weatherly, Intermetallics, 14 (2006) 189-197.
[12] C.Z. Qiu, Y. Liu, L. Huang, W. Zhang, B. Liu, B. Lu, Trans. Nonferrous Met. Soc. China, 22 (2012) 521-527.
[13] K. Hashimoto, H. Doi, K. Kasahara, T. Tsuji, Jpn. J. Inst. Met., 52 (1988) 816-825.
[14] X.J. Jiang, Y.K. Zhou, Z.H. Fujita, H. Mitsui, K. Ishikawa, R. Kainuma, K. Ishida, Acta Mater., 48 (2000) 3113-3123.
[15] V.T. Witusiewicz, A.A. Bondar, U. Hecht, S. Rex, T.Y. Velikanova, J. Alloys Compd., 465 (2008) 64-77.
[16] J. Murray, A. Peruzzi, J. Abriata, J. Phase Equilib., 13 (1992) 277-291.
[17] H. Okamoto, J. Phase Equilib., 14 (1993) 259-260.
[18] A. Peruzzi, J. Nucl. Mater., 186 (1992) 89-99.
[19] G. Batalin, E. Beloborodova, V. Nerubaschenko, V. Galochka, L. Salyukov, Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall, 3 (1982) 74-77.
[20] R. Klein, I. Jacob, P. O’Hare, R. Goldberg, J. Chem. Thermodyn., 26 (1994) 599-608.
[21] S.V. Meschel, O.J. Klepe, J. Alloys Compd., 191 (1993) 111-116.
[22] Y.O. Esin, N. Serebrennikov, E. Pletneva, V. Kapustkin, Izv. Vyssh. Uchebn. Zaved. Chern. Metall., (1986) 1-3.
[23] T.B. Massalski, J. Murray, L. Bennett, H. Baker, American Society for Metals, (1986) 2224.
[24] J. Schuster, J. MSIT Bin. Eval. Progr, (2003).
[25] R. Kematick, I. Jacob, P. O’Hare, R. Goldberg, J. Chem. Thermodyn., 26 (1994) 599-608.
[26] A. Grytsiv, P. Rogl, H. Schmidt, G. Giester, J. Phase Equilib., 24 (2003) 511-527.
[27] V. Kuprina, V. Bernard, A. Grigor’ev, E. Sokolovskaya, I. Kapustkin, Izv. Vyssh. Uchebn. Zaved. Chern. Metall., (1987) 1-3.
[28] I. Ansara, A.T. Dinsdale, M.H. Rand, COST 507, 2 (1998).
[29] I. Ohnuma, Y. Fujita, H. Mitsui, K. Ishikawa, R. Kainuma, K. Ishida, Acta Mater., 48 (2000) 3113-3123.
[30] J. Murray, A. Peruzzi, J. Abriata, J. Phase Equilib., 13 (1992) 277-291.
[31] H. Okamoto, J. Phase Equilib., 14 (1993) 259-260.
[32] A. Peruzzi, J. Nucl. Mater., 186 (1992) 89-99.
[33] G. Batalin, E. Beloborodova, V. Nerubaschenko, V. Galochka, L. Salyukov, Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall, 3 (1982) 74-77.
[34] R. Klein, I. Jacob, P. O’Hare, R. Goldberg, J. Chem. Thermodyn., 26 (1994) 599-608.
[35] Y.O. Esin, N. Serebrennikov, E. Pletneva, V. Kapustkin, Izv. Vyssh. Uchebn. Zaved. Chern. Metall., (1986) 1-3.
[36] T. Wang, Z. Jin, J.-C. Zhao, J. Phase Equilib., 22 (2001) 544-551.
[37] S.N. Tiwari, K. Tangri, J. Nucl. Mater., 32 (1970) 92-96.
AB INIITO I CALPHAD TERMODINAMIČKO ISPITIVANJE Ti–Al–Zr SISTEMA

Z.-X. Deng a,b, D.-P. Zhao c-d, Y.-Y. Huang b, L.-L. Chen b, H. Zou b, Y. Jiang b, K. Chang b-c

aBiološki fakultet, Univerzitet u Hjunanu, Čangša, Hjunan, Kina
bInženjerska laboratorija materijala nuklearne energije, Ningbo institut za tehnologiju i inženjerstvo materijala, Kineska akademija nauka, Zeidžang, Kina

c-dPANDAT Software, version 8.1, CompuTherm LLC, Madison, WI.

Apstrakt

Legure na bazi Ti–Al imaju široku primenu u aeronautici i svemirskoj industriji. Dodavanjem Zr kao legirajućeg elementa može značajno da se poboljša otpornost na visoku temperaturu i koroziju. Da bi se ispitao uticaj koji dodavanje Zr ima na osobine Ti–Al sistema, korišćeni su metodi ab initio proračuna i CALPHAD (proračun faznog dijagrama) da bi se odredio Ti–Al–Zr trojni sistem. Ab initio proračun je izvršen da bi se izračunale entalpije formiranja intermetalnih jedinjenja i krajinjs članova. CALPHAD pristup je primenjen da bi se optimizirali termodinamički parametri zasnovani na eksperimentima. Eksperimentalni podaci fazne ravnoteže pri temperaturama od 1073, 1273, 1473, i 1573 K, kao i vertikalni presek Ti₃Al–Ti + 5 wt.% Zr su korišćeni da bi se ovaj sistem termodinamički optimizovao. Termodinamički parametri binarnih Ti–Al, Al–Zr i Ti–Zr sistema dobijeni su iz nedavno izvršenih optimizacija, a trojni parametri su procenjeni u ovom radu. Utvrđen je set podataka za trojni sistem Ti–Al–Zr, i rezultati proračuna su u skladu sa eksperimentalnim podacima koji se tiču i termodinamičke i fazne ravnoteže.

Ključne reči: Ti–Al–Zr sistem; Ab initio proračun; Fazni dijagrami; Termodinamička optimizacija