Thermodynamic description and phase selection for the Mo–Ti–Zr biomedical alloys

Huaqing Zhang^a, Peng Zhou^{b,*}, Yong Du^{a,*}, Qizhong Huang^{a,*}, Cong Zhang^c,
Libin Liu^d, Shuigen Huang^e, Jozef Vleugels^e

^a State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China

^b Hunan Provincial Key Defence Laboratory of High Temperature Wear-Resisting Materials and Preparation Technology, Hunan University of Science and Technology, Xiangtan, Hunan, 411201, China

^c Collaborative Innovation Center of Steel Technology, University of Science and Technology Beijing, Beijing 100083, China

^d School of Material Science and Engineering, Central South University, Changsha, Hunan, 410083, China

^e KU Leuven, Department of Materials Engineering, B-3001, Heverlee, Belgium

* E-mail: yong-du@csu.edu.cn (Y. Du); zhoupeng1987825@sina.com (P. Zhou)

Abstract:

Thermodynamic information of the Mo–Ti–Zr ternary system is extremely useful to provide guidance for biomedical alloy development. In the present work, the experimental data available from the literature were critically reviewed, and a thermodynamic modeling of the Mo–Ti–Zr system was performed using the CALPHAD (CALculation of PHase Diagram) approach. The solution phases including liquid, bcc_A2 (β) and hcp_A3 (α) were modelled by the substitutional solution model, and the laves_C15 phase was modelled using a two sublattice model. In the Mo–Ti–Zr system, there is no ternary compound. A set of self-consistent thermodynamic parameters were developed. Comprehensive comparisons between the calculated and measured phase diagrams suggest that the experimental information is satisfactorily accounted for by the present thermodynamic modelling. The discrepancies between the calculated and measured phase equilibria have been well explained in this work. With regard to the β phase, the miscibility gap and related phase relations are well described by the present calculation. The liquidus projection and Scheil solidification simulation were generated using the present thermodynamic parameters. The presently calculated phase diagrams of the Mo–Ti–Zr alloys can be used in the biomedical field. Based on the calculations in the present work, two guidelines were formulated to avoid the laves phase formation in these frequently studied Mo–Ti–Zr biomedical alloys.

Keywords: Mo–Ti–Zr biomedical alloys; Phase diagram; Thermodynamic calculation; Liquidus projection; Scheil solidification simulation

1. Introduction

The Mo–Ti–Zr ternary system is of great interest because it is an important sub-system in Mo-based and Ti-based alloys. Mo-based alloys have a wide application range in aerospace, nuclear and electronic industries owing to their favourable high temperature properties^[1,2]. Amongst different Mo-based alloys, titanium-zirconium-molybdenum (TZM, 0.5 ~ 0.8 wt.% Ti, 0.08 ~ 0.1 wt.% Zr, 0.016 ~ 0.02 wt.% C) alloy exhibits a high melting temperature, superior creep and tensile strength at high temperatures, low coefficient of thermal expansion and excellent corrosion resistance in liquid metals^[3-7]. Ti-based alloys have extensive applications in the biomedical field due to their good corrosion resistance, high specific mechanical strength, relatively low elastic modulus and excellent biocompatibility^[8-11]. The addition of Mo and Zr elements into titanium alloys can decrease the Young's modulus and improve corrosion resistance, mechanical strength and biocompatibility^[12,13]. Moreover, addition of secondary carbides Mo₂C, ZrC, NbC and WC in Ti(C,N)-based cermets is known to improve the mechanical properties and produce advanced cutting materials. It is of interest to establish a thermodynamic database for Ti(C,N)-based cermets to guide the manufacturing process or design advanced cermet materials^[14,15]. The establishment of such a thermodynamic database requires the experimental data of the Mo–Ti–Zr^[16] and some relevant systems^[17-20]. The knowledge of phase equilibria and thermodynamic modelling of the Mo–Ti–Zr system is important to perform TZM or Ti-based biomedical alloy design and establish a thermodynamic database for Ti(C,N)-based cermets.

Extensive phase diagram data of the Mo–Ti–Zr system are available in the literature^[16,21-28]. Kar et al.^[29] optimized the Mo–Ti–Zr system incompletely, and excluded the miscibility gap in the bcc_A2 phase. Since a reliable thermodynamic description for the whole Mo–Ti–Zr system is still unavailable in the literature, the present work aims to obtain a set of self-consistent thermodynamic parameters for the ternary system by means of the CALPHAD approach and provide a guidance for Mo–Ti–Zr biomedical alloys design. Nowadays, many biomedical alloys are developed by pure experimental approaches. It is highly expected the thermodynamic calculation can guide the development of the biomedical alloy efficiently. The symbols to denote the stable phases in the Mo–Ti–Zr system are summarized in Table 1 for facilitating reading.

1.1 Binary systems

The Mo–Ti system has no intermediate compounds and there are liquid, bcc and hcp solution phases.

The miscibility gap in the bcc phase was determined by Terauchi et al.^[30] over a composition range 0.2-0.48 at.% Mo at 948 to 1068 K and a invariant reaction (monotectoid reaction, bcc $\rightarrow$ hcp + bcc) was reported to occur at 948 K. Then the temperature of the monotectoid reaction was measured at 968 K by McAlister^[31] via differential thermal analysis measurement. Recent thermodynamic assessments of the Mo–Ti system were carried out by Shim et al.^[32], Ansara et al.^[33] and Chung et al.^[34].

In the present work, the miscibility gap in the bcc phase is considered and the thermodynamic parameters for the Mo–Ti system are taken from Chung et al.^[34]. Fig. 1(a) presents the calculated Mo–Ti phase diagram. The Mo–Zr phase diagram assessed by Pérez and Sundman^[35] and the Ti–Zr phase diagram assessed by Kumar et al.^[36] are adopted in this work and are reproduced in Fig. 1(b) and (c), respectively.

1.2 Mo–Ti–Zr ternary system

The Mo–Ti–Zr ternary system was previously reviewed by Eremenko and Tretyachenko^[37] and Watson^[38]. Besides the experimental phase diagram data included in the reviews, the data not included or published later or are considered in the present work. The main contribution to the Mo–Ti–Zr experimental phase diagrams comes from the work by Chuang et al.^[28], Prokoshkin and Zakharova^[21-23], Zakharov and Savitskii^[26], Zakharova and Prokoshkin^[24], Kudryavtsev and Tararaeva^[27], Khagai and Budberg^[25], and Zhang et al.^[16].

Chuang et al.^[28] investigated the isothermal section at 1473 K for the Mo–Ti–Zr ternary system using X-ray diffraction (XRD), optical microscopy (OM), hardness and microhardness. According to Chuang et al.^[28], a single phase β (bcc solid solution) and two-phase region β + laves (Mo_2Zr) exist in the isothermal section. However, their results^[28] are inconsistent with the isothermal section at 1473 K reported by Prokoshkin and Zakharova^[23], whose results show a miscibility gap ($\beta_1 + \beta_2$, β_1 is rich in Mo, Ti and β_2 is rich in Ti, Zr) in the β phase and the solubility of Ti in Mo_2Zr can be up to 21 at.%. In the present work, the data reported by Chuang et al.^[28] are used to optimized the phase boundary (β / β + laves) of the isothermal section at 1473 K.

By means of XRD, OM, hardness and microhardness, Prokoshkin and Zakharova^[21-23] measured the isothermal sections at 1473, 1173, 1073, 1023 and 873 K. The characteristics of these isothermal sections were described in detail by Zhang et al.^[16]. Based on these isothermal sections data and differential thermal analysis (DTA) measurement, Zakharova and Prokoshkin^[24] constructed three vertical sections at 10, 20 and 30 at.% Ti. They also described an invariant reaction: $L + \beta_1 \rightarrow \beta_2 + \text{laves}$ at 1848 K, which is consistent with the result of Prokoshkin and Zakharova^[21]. The invariant equilibrium was considered as a reliable one and performed in the present modelling.

Using XRD, microhardness and optical pyrometer methods, Zakharov and Savitskii^[26] studied the isothermal sections at 1773 and 1273 K, vertical sections at 10 and 30 wt.% Ti, $w(\text{Mo}):w(\text{Zr}) = 2.1:1$ and $1:3$, and liquidus projection. According to their experimental data, the β phase does not separate into two phases (β_1 and β_2) and there is no solubility in the binary laves (Mo_2Zr) phase, which are inconsistent with other reported data^[16,21-25]. Therefore, the experimental data from Zakharov and Savitskii^[26] were not used in this work.

Kudryavtsev and Tararaeva^[27] investigated the phase diagrams (isothermal sections at 1573, 1473, 1373, 1273, 1173, 1073, 973 and 873 K, vertical sections at $w(\text{Mo}):w(\text{Ti}) = 4:1$, $1:1$ and $1:4$) in the Zr rich corner for the Mo–Ti–Zr system based on OM, hardness and microhardness measurements. Khagai and Budberg^[25] reported a vertical section from pure Ti to Mo_2Zr using microscopy (optical and electronic),

XRD and optical pyrometry methods. The results are not taken into account in the present assessment since the vertical section constructed by Khegay and Budberg^[25] violates Schreinemakers' rule^[39]. Zhang et al.^[16] experimentally determined the isothermal sections at 1373, 1173 K and liquidus projection by means of XRD, OM and electron probe microanalysis (EPMA). The alloys used for the determination were arc melted and annealed at 1373 and 1173 K for 20 and 40 days, respectively. However, the measured phase compositions at 1173 K by Zhang et al.^[16] are inconsistent with the previous data^[23]. According to Prokoshkin and Zakharova^[21-23], the annealing time of the alloys at low temperatures (below 1173 K) was too short to reach equilibrium. The slow diffusion of refractory Mo and Zr^[40,41] may hinder the equilibration process at low temperatures, so the alloys need a long time to achieve thermodynamic equilibrium. Therefore, the experimental results from Zhang et al.^[16] and the data reported by Prokoshkin and Zakharova^[21-23], Kudryavtsev and Tararaeva^[27] at high temperatures were adopted in the present work.

The evaluation of the available experimental data pertaining to the Mo–Ti–Zr system is summarized in Table 2, together with an indication whether the data were used or not.

2. Thermodynamic models

In this modelling, the Gibbs energy functions for pure elements Mo, Ti and Zr were taken from the SGTE compilation by Dinsdale^[42].

2.1 Liquid and solid solution phases

The liquid and solid solution phases (bcc and hcp) are described as substitutional solutions, and the Gibbs energy of each solution phase is expressed by the Redlich–Kister–Muggianu polynomial^[43,44].

$$\begin{aligned}
 {}^0G_m^\phi &= x_{\text{Mo}} {}^0G_{\text{Mo}}^\phi + x_{\text{Ti}} {}^0G_{\text{Ti}}^\phi + x_{\text{Zr}} {}^0G_{\text{Zr}}^\phi \\
 &+ RT(x_{\text{Mo}} \ln x_{\text{Mo}} + x_{\text{Ti}} \ln x_{\text{Ti}} + x_{\text{Zr}} \ln x_{\text{Zr}}) \\
 &+ x_{\text{Mo}} x_{\text{Ti}} L_{\text{Mo, Ti}}^\phi + x_{\text{Mo}} x_{\text{Zr}} L_{\text{Mo, Zr}}^\phi + x_{\text{Ti}} x_{\text{Zr}} L_{\text{Ti, Zr}}^\phi + {}^{\text{ex}}G_{\text{Mo, Ti, Zr}}^\phi
 \end{aligned} \tag{1}$$

where x_i is the mole fraction of element i ($i = \text{Mo, Ti and Zr}$), ${}^0G_i^\phi$ is the Gibbs energy of element i in the ϕ phase (ϕ : Liquid, bcc and hcp) and R is the gas constant. The second term in Eq. (1) is the contribution to the Gibbs energy from the ideal entropy of mixing. $L_{\text{Mo, Ti}}^\phi$, $L_{\text{Mo, Zr}}^\phi$ and $L_{\text{Ti, Zr}}^\phi$ in Eq. (1) are interaction parameters from the binary systems^[32,35,36]. The ternary excess Gibbs energy ${}^{\text{ex}}G_{\text{Mo, Ti, Zr}}^\phi$ in Eq. (1) is expressed as:

$${}^{\text{ex}}G_{\text{Mo, Ti, Zr}}^\phi = x_{\text{Mo}} x_{\text{Ti}} x_{\text{Zr}} (x_{\text{Mo}} \cdot {}^0L_{\text{Mo, Ti, Zr}}^\phi + x_{\text{Ti}} \cdot {}^1L_{\text{Mo, Ti, Zr}}^\phi + x_{\text{Zr}} \cdot {}^2L_{\text{Mo, Ti, Zr}}^\phi) \tag{2}$$

where ${}^0L_{\text{Mo, Ti, Zr}}^\varphi$, ${}^1L_{\text{Mo, Ti, Zr}}^\varphi$ and ${}^2L_{\text{Mo, Ti, Zr}}^\varphi$ in Eq. (2) are the ternary parameters to be evaluated in the present work.

2.2 Laves phase

The laves phase (Mo_2Zr) exhibits an extended solubility for Ti in the Mo–Ti–Zr ternary system. In view of the large solubility for Ti in the laves phase, the sublattice model $(\text{Mo, Ti, Zr})_2(\text{Mo, Ti, Zr})_1$ is used in this work, and its Gibbs energy per mole of formula can be described as:

$$G_m^{\text{laves}} = \sum_i \sum_j y'_i y''_j {}^0G_{i,j}^{\text{laves}} + RT(2 \sum_i y'_i \ln y'_i + \sum_i y''_i \ln y''_i) + \sum_i \sum_j \sum_k (y'_i y'_j y''_k L_{i,j,k}^{\text{laves}} + y'_i y''_j y''_k L_{i,j,k}^{\text{laves}}) \quad (3)$$

where y'_i and y''_j are the site fractions of species i on the first and j on the second sublattices for the model $(\text{Mo,Ti,Zr})_2(\text{Mo,Ti,Zr})_1$, respectively. ${}^0G_{i,j}^{\text{laves}}$ represents the Gibbs energy of hypothetical end members, i.e. i_2j compound with the laves structure. The parameters $L_{i,j,k}^{\text{laves}}$ and $L_{i,j,k}^{\text{laves}}$ represent the Gibbs energy contribution from interactions between different components within the first and second sublattice, respectively.

2.3. Computational method

All calculations were conducted using Thermo-Calc software. The assessment of the model parameters in the Mo–Ti–Zr ternary system has been carried out by recurrent runs of the PARROT module^[45], which works by minimizing the sum of the square of the differences between measured and calculated values. The step-by-step optimization procedure described by Du et al.^[46] was utilized in the present calculation. Each piece of selected experimental information was given a certain weight according to the uncertainties of the experimental data. The weights were varied systematically during the optimization process to have the best thermodynamic description for the Mo–Ti–Zr ternary system.

The optimization of Mo–Ti–Zr system began with solid phases using the experimental data from literature^[16,21-24,27,28]. Since most experimental data^[16,21-24] concern the solubility of laves phase, the thermodynamic parameters for this phase were assessed firstly. Two parameters ${}^0G_{\text{Mo:Ti}}^{\text{laves_C15}}$ and ${}^0G_{\text{Ti:Zr}}^{\text{laves_C15}}$ were evaluated to be large positive values to avoid the stabilization of laves phase in the Mo–Ti and Ti–Zr binary systems. The ternary parameter ${}^0L_{\text{Mo, Ti: Zr}}^{\text{laves_C15}}$ was optimized according to the experimental solubility data of Ti in the Mo_2Zr phase. The parameters for the laves phase were then fixed in the subsequent optimization steps. Secondly, the bcc phase

was introduced in the calculation. Three ternary parameters ${}^0L_{\text{Mo, Ti, Zr: Va}}^{\text{bcc_A2}}$, ${}^1L_{\text{Mo, Ti, Zr: Va}}^{\text{bcc_A2}}$ and ${}^2L_{\text{Mo, Ti, Zr: Va}}^{\text{bcc_A2}}$ for the bcc phase were employed to reproduce the ternary miscibility gap extending from the Mo–Ti system and fit the phase boundary (β / β + laves) from isothermal sections in this work. Thirdly, the vertical sections^[24], liquidus projection^[16] and invariant equilibria^[24] data were taken into account. In this process, the parameters ${}^0L_{\text{Mo, Ti, Zr}}^{\text{Liquid}}$, ${}^1L_{\text{Mo, Ti, Zr}}^{\text{Liquid}}$ and ${}^2L_{\text{Mo, Ti, Zr}}^{\text{Liquid}}$ of the liquid phase were optimized to reproduce the experimental data. Finally, the parameters obtained at each step were optimized simultaneously by taking into account all the reliable data mentioned previously. Over the whole calculation procedure, we found that the hcp parameters from the modelling of binary systems are adequate to describe the phase equilibria of the Mo–Ti–Zr system and thus no additional hcp parameters were introduced.

3. Results and discussion

The thermodynamic parameters describing the Mo–Ti–Zr system are listed in Table 3, where the parameters optimized in the present modelling are underlined. Using this set of parameters, a series of phase diagrams, including isothermal sections, vertical sections, liquidus projection and Scheil solidification curves were calculated to show the rationality of the present modelling.

Figure 2 shows the calculated isothermal sections of the Mo–Ti–Zr system at 1673, 1573, 1473, 1373, 1273, 1173, 1073, 1023 and 873 K in comparison with the experimental data^[16,21-24,27,28]. Fig. 2 shows a good overall agreement between the calculated phase diagrams and the experimental data within the estimated experimental uncertainties. The solubility of Ti in the laves phase increases with temperature.

Fig. 2(a) presents the calculated isothermal section at 1673 K in comparison with the experimental data reported by Zakharova and Prokoshkin^[24]. Most of the experimental data can be satisfactorily accounted for by the present calculation, except for the β / β_1 (β_2) + laves phase boundaries. However, the phase boundary (β / β_2 + laves) data in the Zr-rich corner reported by Kudryavtsev and Tararaeva^[27] are well reproduced by the present calculation, as shown in Fig. 2(b)-(g). As temperature decreases, the three-phase region β_1 + laves + β_2 in these calculated isothermal sections becomes larger.

Fig. 2(f) compares the calculated isothermal section at 900 °C with the experimental data^[16,24,27]. The calculated results can reasonably reproduce most of the experimental data. Figs. 2(h) and (i) compare the calculated isothermal sections at 1023 and 873 K with the experimental data^[22,24,25,27], respectively. There are discrepancies between the calculated and measured phase equilibrium. The discrepancies are caused by three reasons: (i) The binary phase diagrams were used in the literature^[21,22,24,25,27] and adopted in the present work are different, especially for the Mo–Ti system, which may result in misinterpretation of the phase relation in the ternary region. (ii) Limited by experimental techniques in the early time, this make

them^[21,22,24] very difficult to accurately determine the phase boundaries of the miscibility gap. (iii) The short annealing time was adopted in the literature^[21,22,24] cannot guarantee that these alloys reach thermodynamic equilibrium at low temperatures. All attempts to reduce these discrepancies and get a better fit with the measured data resulted in a deterioration of the overall agreement.

Fig. 3 presents the calculated vertical sections at constant Ti contents of 10, 20 and 30 at.% in comparison with the experimental data reported by Zakharova and Prokoshkin^[24]. Fig. 4 shows the calculated vertical sections at $w(\text{Mo}):w(\text{Ti}) = 4:1, 1:1$ and $1:4$ with the experimental values from Kudryavtsev and Tararaeva^[27]. In Figs. 3 and 4, except for the experimental data at 1023 and 873 K, most of the experimental values can be well accounted within the estimated errors.

The calculated liquidus projection of the Mo–Ti–Zr system is shown in Fig. 5 and compared with experimental data^[16,26]. In Fig. 5, there is an invariant reaction $L + \beta_1 \rightarrow \beta_2 + \text{laves}$ at 1829 K. The invariant reaction type and temperature reported in literature^[24] are reproduced by the present work. The calculated temperature for the critical point, which is associated with the ternary miscibility gap on the liquidus surface, is 1940 K. Considering the larger experimental uncertainty (± 25 K) for the critical point, the calculated temperature of the critical point can also be accepted in this optimization.

4. Application

Ti–6Al–4V^[10,11] alloy is one of the most frequently used implant materials in the biomedical field. The elastic modulus of Ti–6Al–4V alloy is 110 GPa, much higher than that of human bone (10–40 GPa)^[47]. It was reported that β -type Mo–Ti–Zr alloys with relatively low elastic modulus have been considered as promising candidates to replace Ti–6Al–4V alloy for use as biomaterials. In order to develop alloys with good mechanical properties and biocompatibility, the microstructure and properties of Mo–Ti–Zr alloys with different compositions and different heat treatment conditions were investigated^[48–56]. Table 4 lists the heat treatment conditions and phases of Mo–Ti–Zr alloys for biomedical applications. There are three metastable phases (α' : distorted hexagonal structure, α'' : orthorhombic structure and ω : metastable phase trigonal or hexagonal structure^[56,57]), which do not exist in the stable phase diagrams.

To facilitate reading, a schematic diagram illustrating the composition ranges of Mo–Ti–Zr alloys used in the biomedical field is presented in Fig. 6. As known, the β phase in Ti-based biomaterials exhibits a low Young's modulus^[9] and β -type titanium alloys satisfy most of the other requirements for metallic biomaterials. The vertical sections at 12 at.%, 12 and 15 wt.% Mo, 10, 15, 20 and 30 wt.% Zr were calculated to ascertain the phase regions and phase transition temperatures of β and α phases in Mo–Ti–Zr biomedical alloys. The calculated vertical sections at 12 at.%, 12 and 15 wt.% Mo, 10, 15, 20 and 30 wt.% Zr with the selected alloy compositions^[48–56] are shown in Fig. 7 and Fig. 8, respectively. Nie et al.^[51] investigated 12 at.% Mo– x Ti–Zr ($x=0, 3, 7$ and 11 at.%) alloys to develop new biomaterials for hard tissue replacements. They prepared these samples by vacuum arc melting method and the results show that all the as-cast alloys consist of β phase.

The Scheil solidification simulation is a very effective method to predict crystallisation sequences and phase constitution during cooling. The structures and the compositions of the various phases which precipitate can affect casting properties^[58], microstructures and mechanical properties^[59]. However, it is difficult to determine the crystallisation sequences through microstructure analysis. In the present work, the calculated Scheil solidification curves for these alloys are presented in Fig. 9(a). The Scheil simulation exhibits the primary phase and solidification path for the four alloys. It can be seen from the curves that the primary phase is β and the solidification path is $L \rightarrow L + \text{bcc} \rightarrow L + \text{bcc} + \text{Laves}$. Since the content of the laves phase is small, Nie et al.^[51] did not detect the laves phase in these alloys. Our calculations can describe the phases observed by Nie et al.^[51].

The strength of biomedical alloys is also an important factor in their long-term use as orthopedic prostheses, dental implants, etc. for biomedical applications. The intermetallic compound laves phase exhibits excellent high temperature performance, but it is a brittle phase at room temperature due to its complex crystal structure^[60,61]. Cr_2Nb , Cr_2Ti , Cu_2Mg , Cr_2Ta , Fe_2Ti and other laves phases also have the characteristic^[60–63]. The service temperature of biomedical alloys is close to room temperature, laves phase should be avoided in Mo–Ti–Zr biomedical alloys. However, the Zr-rich materials selected by Nie et al.^[51] are located in the phase regions containing laves phase, as shown in Fig. 7(a), which indicates that the laves phase will appear in these alloys after heat treatment such as annealing. The composition for heat-treated alloys can be chosen from the left side of Fig. 7(a) to avoid the existence of laves phase. Fig. 7(b) and (c) depicts the vertical sections at 12 and 15 wt.% Mo, respectively. Several literature reports^[48,50,52–56] addressed Mo–Ti–Zr biomedical alloys compositions on the Zr-poor side. Zhao et al.^[48] fabricated a 12Mo–Ti–5Zr (wt.%) alloy, which was homogenized at 1273 K for 10 h and subjected to solution treatment (ST) at 1133 and 1053 K for 1 h, respectively. Their results^[48] suggest that there are α and $\beta + \alpha''$ phases in the alloy after different heat treatments, as shown in Table 4. However, the calculated stable phase diagram for the 12Mo–Ti–5Zr (wt.%) alloy in Fig. 7(b) indicates that only β phase exists at 1273, 1133 and 1053 K. Due to the martensitic transformation in the Mo–Ti–Zr alloy, the β phase completely converted to α phase at 1273 K and partially converted to α'' phase at 1133 and 1053 K. The Scheil simulation for 15 wt.% Mo–Ti– x Zr ($x = 5, 10$ and 15 wt.%) alloys is shown in Fig.9(b). The primary phase is β and the solidification path is $L \rightarrow L + \text{bcc}$, which agrees with the reported results^[50,53,54].

The calculated vertical sections at constant Zr contents show that there is laves phase in the Ti-rich portion at low temperatures, as shown in Fig. 8. The presence of laves phase is detrimental to the properties of Mo–Ti–Zr biomedical alloys, as described above. Therefore, the alloys chosen in [49,50,52–56] should not be heat treated at low temperatures to avoid the emergence of laves phase.

5. Conclusions

The ternary Mo–Ti–Zr system was thermodynamically described, taking into account the miscibility gap in the β phase. A set of self-consistent thermodynamic parameters for the Mo–Ti–Zr system was obtained. The isothermal sections, vertical sections, liquidus projection and Scheil solidification curves were calculated. Comprehensive comparisons showed that most of experimental phase diagram data can be well described by the present calculations. The discrepancies between the calculation results and experimental data are attributed to the use of different binary systems in the literature and this work, limited experimental conditions in the early time and short annealing time for the Mo–Ti–Zr alloys at low temperatures, which require further experimental verification by performing key experiments in combination with current calculation results.

It is of high interest to apply the present thermodynamic modeling for the phase selection of Mo–Ti–Zr biomedical alloys. According to the calculation results, there are two guidelines, which can be used for the phase selection of these frequently studied Mo–Ti–Zr biomedical alloys:

- To avoid the presence of laves phase in the alloys with 12 at.% Mo, the composition for heat-treated alloys can be chosen from the Ti-rich corner.
- The alloys with constant Zr contents of 10, 15, 20 and 30 wt.% should not be heat treated at low temperatures to avoid the laves phase.

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Figures:

Fig. 1. Calculated binary phase diagram: (a) Mo-Ti system^[34], (b) Mo-Zr system^[35], (c) Ti-Zr system.^[36]

(a) T = 1400 °C

(b) T = 1300 °C

(c) T = 1200 °C

(d) T = 1100 °C

(e) T = 1000 °C

(f) T = 900 °C

(g) T = 800 °C

(h) T = 750 °C

Fig. 2 Calculated isothermal sections for the Mo–Ti–Zr system at (a) 1400 °C, (b) 1300 °C, (c) 1200 °C, (d) 1100 °C, (e) 1000 °C, (f) 900 °C, (g) 800 °C, (h) 750°C and (i) 600 °C together with the experimental data.^[16,21-28]

Fig. 3 Calculated vertical sections of the Mo–Ti–Zr system at (a) 10 (b) 20 and (c) 30 at.% Ti, compared with experimental data reported by Zakharova and Prokoshkin.^[24]

Fig. 4 Calculated vertical sections of the Mo-Ti-Zr system at w(Mo):w(Ti)=(a) 4:1, (b) 1:1 and (c) 1:4, in comparison with experimental data reported by Kudryavtsev and Tararaeva.^[27]

Fig. 5 Calculated liquidus projection in the Mo–Ti–Zr system in comparison with the experimental data.^[16,26]

Fig. 6 Schematic diagram illustrating the composition ranges of Mo–Ti–Zr alloys used in the biomedical field.

Fig. 7 Calculated vertical sections at (a) 12 at.% Mo, (b) 12 wt.% Mo and (c) 15 wt.% Mo with the literature alloy compositions^[48,51-56] indicated by the vertical lines.

Fig. 8 Calculated vertical sections at (a) 10 (b) 15, (c) 20 and (d) 30 wt.% Zr with the literature alloy compositions^[49,50,52-56] indicated by the vertical lines.

Fig. 9 Scheil-simulation for (a) 12 at.% and (b) 15 wt.% Mo alloys.

Table 1 List of the symbols to denote the phase in the Mo–Ti–Zr system

Phase	Pearson's symbol, Space group	TDB designation	Phase description
β^a	cI2, Im-3m	bcc_A2	Continuous solid solution based on bcc (Mo, Ti, Zr)
α	hP2, P6 ₃ /mmc	hcp_A3	Solid solution based on hcp (α Ti) and (α Zr)
laves	cF24, Fm-3d	laves_C15	Intermediate compound based on Mo ₂ Zr
Liquid	-	Liquid	Liquid solution

^a There is a miscibility gap in the β phase, subscripts are used to distinguish the composition sets by, i.e. β_1 denotes Mo, Ti rich composition, β_2 denotes Ti, Zr rich ones.

Table 2 Summary of the experimental phase equilibria in the Mo–Ti–Zr ternary system

Type of experimental data	Experimental technique ^(a)	Quoted mode ^(b)	References
Isothermal section at 1473 K	XRD, OM, HM, MM	■	[28]
Isothermal sections at 1473, 1173, 1073, 1023 and 873 K	XRD, OM, HM, MM	○	[21-23]
Isothermal sections at 1773 and 1273 K; Vertical sections at 10 and 30 wt.% Ti, w(Mo):w(Zr) = 2.1:1 and 1:3, and liquidus projection	XRD, MM, OP	∅	[26]
Vertical sections at 10, 20 and 30 at.% Ti and an invariant reaction temperature	XRD, OM, HM, MM, DTA	○	[24]
Zr-rich isothermal sections at 1573, 1473, 1373, 1273, 1173, 1073, 973 and 873 K; Vertical sections at w(Mo):w(Ti) = 4:1, 1:1 and 1:4	OM, HM, MM	○	[27]
Vertical section of Mo ₂ Zr-Ti	OM, EM, XRD, OP	∅	[25]
Isothermal sections at 1373 and 1173 K, and liquidus projection	XRD, OM, EPMA	■	[16]

^(a) For the experimental techniques: XRD: X-ray diffraction, OM: optical microscopy, HM: hardness measurement, MM: microhardness measurement, OP: optical pyrometry, DTA: differential thermal analysis, EM: electron microscopy, EPMA: electron probe microanalysis.

^(b) Indicates whether the data were used or not in the optimization process: ■ used; ○ partially used; ∅ not used.

Table 3 Summary of the calculated thermodynamic parameters in the Mo–Ti–Zr system^a

Liquid: Model (Mo, Ti, Zr) ₁
${}^0L_{\text{Mo, Ti}}^{\text{Liquid}} = -17494.7 - 3.57111T$
${}^1L_{\text{Mo, Ti}}^{\text{Liquid}} = -463.9 + 9.0476T$
${}^0L_{\text{Mo, Zr}}^{\text{Liquid}} = -24055.12 + 8.146158T$
${}^1L_{\text{Mo, Zr}}^{\text{Liquid}} = -5132.1665 + 4.8041224T$
${}^0L_{\text{Ti, Zr}}^{\text{Liquid}} = -968$
${}^0L_{\text{Mo, Ti, Zr}}^{\text{Liquid}} = \underline{-80000}$
${}^1L_{\text{Mo, Ti, Zr}}^{\text{Liquid}} = \underline{180000}$
${}^2L_{\text{Mo, Ti, Zr}}^{\text{Liquid}} = \underline{-35000}$
bcc_A2: Model (Mo, Ti, Zr) ₁ : (Va) ₃
${}^0L_{\text{Mo, Ti: Va}}^{\text{bcc_A2}} = 3383.4 - 10.0774T$
${}^1L_{\text{Mo, Ti: Va}}^{\text{bcc_A2}} = -56704.6 + 32.12T$
${}^2L_{\text{Mo, Ti: Va}}^{\text{bcc_A2}} = -15172.4$
${}^0L_{\text{Mo, Zr: Va}}^{\text{bcc_A2}} = 17935.985 + 3.102T$
${}^1L_{\text{Mo, Zr: Va}}^{\text{bcc_A2}} = -990.9911 + 4.299T$
${}^0L_{\text{Ti, Zr: Va}}^{\text{bcc_A2}} = -4346 + 5.489T$
${}^0L_{\text{Mo, Ti, Zr: Va}}^{\text{bcc_A2}} = \underline{-30595 + 55T}$
${}^1L_{\text{Mo, Ti, Zr: Va}}^{\text{bcc_A2}} = \underline{-134760 + 116T}$
${}^2L_{\text{Mo, Ti, Zr: Va}}^{\text{bcc_A2}} = \underline{227300 - 143.6T}$
hcp_A3: Model (Mo, Ti, Zr) ₁ : (Va) _{0.5}
${}^0L_{\text{Mo, Ti: Va}}^{\text{hcp_A3}} = 14250.8$

$${}^0L_{\text{Mo, Zr: Va}}^{\text{hcp_A3}} = 26753.79 + 4.556T$$

$${}^0L_{\text{Ti, Zr: Va}}^{\text{hcp_A3}} = 5133$$

laves_C15: Model (Mo, Ti, Zr)₂: (Mo, Ti, Zr)₁

$${}^0G_{\text{Mo: Mo}}^{\text{laves_C15}} - 3 {}^0G_{\text{Mo}}^{\text{bcc_A2}} = 15000$$

$${}^0G_{\text{Ti: Ti}}^{\text{laves_C15}} - 3 {}^0G_{\text{Ti}}^{\text{hcp_A3}} = \underline{15000}$$

$${}^0G_{\text{Zr: Zr}}^{\text{laves_C15}} - 3 {}^0G_{\text{Zr}}^{\text{hcp_A3}} = 15000$$

$${}^0G_{\text{Mo: Ti}}^{\text{laves_C15}} - 2 {}^0G_{\text{Mo}}^{\text{bcc_A2}} - {}^0G_{\text{Ti}}^{\text{hcp_A3}} = \underline{15000}$$

$${}^0G_{\text{Ti: Zr}}^{\text{laves_C15}} - 2 {}^0G_{\text{Ti}}^{\text{hcp_A3}} - {}^0G_{\text{Zr}}^{\text{hcp_A3}} = \underline{15000}$$

$${}^0G_{\text{Mo: Zr}}^{\text{laves_C15}} - 2 {}^0G_{\text{Mo}}^{\text{bcc_A2}} - {}^0G_{\text{Zr}}^{\text{hcp_A3}} = -21734.78 + 0.1441789T$$

$${}^0G_{\text{Zr: Mo}}^{\text{laves_C15}} - {}^0G_{\text{Mo}}^{\text{bcc_A2}} - 2 {}^0G_{\text{Zr}}^{\text{hcp_A3}} = -21734.78 + 0.1441789T$$

$${}^0L_{\text{Mo, Zr: *}}^{\text{laves_C15}} = 100000$$

$${}^0L_{\text{*: Mo, Zr}}^{\text{laves_C15}} = 60000$$

$${}^0L_{\text{Mo, Ti: Zr}}^{\text{laves_C15}} = \underline{50604 - 60.8T}$$

^a All parameters are given in J/mole and temperature (T) in K. The Gibbs energies for the pure elements are from the SGTE compilation^[42]. The thermodynamic parameters in the Mo–Ti, Mo–Zr and Ti–Zr systems were taken from Chung et al.^[32], Pérez and Sundman^[35], Kumar et al.^[36], respectively. The underlined parameters were assessed in the present work.

Table 4 Summary of the heat treatment conditions and phases of Mo–Ti–Zr alloys for biomedical application

Nominal composition		Heat treatment	Phase ^a	Ref.
Mo	Zr			
12 wt. %	5 wt. %	Homogenized at 1273 K, 10 h; Solution treatment (ST) at 1133 and 1053 K, 1 h	α (Homogenized) $\beta + \alpha''$ (1133 K) $\beta + \alpha''$ (1053 K)	[48]
0 wt. %	30 wt. %	Homogenized at 1373 K, 6h, then hot rolled at 1273 K and ST at 1123 K, 1 h	α'	[49]
2 wt. %	30 wt. %		$\beta + \alpha'$	
5, 6 and 7 wt. %	30 wt. %		$\beta + \omega$	
8 wt. %	30 wt. %		β	
0 and 1 wt. %	10 wt. %		α'	
3 wt. %	10 wt. %		$\alpha' + \alpha''$	
5 wt. %	10 wt. %		α''	
7.5 wt. %	10 wt. %	As cast	$\beta + \omega$	[50]
10, 12.5, 15, 17.5 and 20 wt. %	10 wt. %		β	
12 at. %	88, 85, 81 and 77 at. %		β	
5 wt. %	15 wt. %		$\beta + \alpha' + \alpha''$	
10 wt. %	15 wt. %	Homogenized at 1273 K, 24 h and hot rolled at 1273 K	$\beta + \alpha''$	[52]
15 and 20 wt. %	15 wt. %		β	
15 wt. %	5, 10 and	As cast	β	[53]

	15 wt. %		
5 and 10 wt. %	15 wt. %		$\beta + \alpha''$
15 wt. %	15 wt. %		β
0 wt. %	20 wt. %		α
2.5 wt. %	20 wt. %	As cast	$\alpha' + \alpha''$
5 and 7.5 wt. %	20 wt. %		$\beta + \alpha''$ [54]
10 wt. %	20 wt. %		β
0 wt. %	15 wt. %		α
5 wt. %	15 wt. %		$\beta + \alpha' + \alpha''$ (as-cast and 873 K, 24h);
		As cast	$\beta + \alpha'$ (873 K, 6h and 12h)
10 wt. %	15 wt. %	873 K, 6 h, 12h and 24h, cooling rate: 10 °C/min.	$\beta + \alpha'$ [55]
15 wt. %	15 wt. %		β (as cast); $\beta + \alpha'$ (873 K, 6h and 24h); $\beta + \alpha' + \alpha''$ (873 K, 12h)
0 wt. %	15 wt. %		α'
2.5, 5 and 7.5 wt. %	15 wt. %	Hot rolled at 1273 K	$\beta + \alpha' + \alpha''$
10 wt. %	15 wt. %		$\beta + \alpha''$ [56]
12.5, 15 and 20 wt. %	15 wt. %		β

^a β : bcc; α : hcp; α' : distorted hexagonal structure α'' : martensite phase (orthorhombic structure); ω : metastable phase trigonal or hexagonal structure