1. Introduction

Currently, research on biomedical applications, specifically load-bearing implants, focuses on finding a suitable, high strength and low Young's modulus ($E$) implant that has long term biocompatibility and good corrosion resistance [1,2]. In recent years, titanium (Ti) alloys have attracted great interest for a wide assortment of biomedical applications, including being used in load-bearing implants. This is due to the fact that Ti, which is biocompatible, can be alloyed with other biocompatible elements and retain a high strength but have a lower Young's modulus [1-4]. One of the main things to consider when selecting a Ti-alloy for an implant material is phase stability. Ti is stable in the $\alpha$ (hexagonal close packed, hcp) phase below 1155 K under standard pressure, but transforms to the $\beta$ (body centered cubic, bcc) phase above 1155 K. The bcc phase can be stabilized by alloying with $\beta$-stabilizers and such bcc Ti alloys have received much attention because of their low $E$ values. Ti in the hcp phase has a $E$ of 105 GPa while, the Ti-35 Nb-STa-7Zr alloy in the bcc phase has a $E$ of 55 GPa which is more comparable to that of bone (~10-40 GPa) [1,5-7]. Several bcc phase alloys with a lower Young’s modulus have been developed, such as Ti-13 Nb-13Zr, Ti-35 Nb-STa-7Zr-0.4 O, Ti-29 Nb-Ta-Zr, and Ti-25 Nb-Ta-Zr with their Young’s moduli between 71 and 57 GPa [1,8,9]. Elements such as Mo, Nb and Ta are all biocompatible elements and strong $\beta$-stabilizers, while Zr is a biocompatible weak $\beta$-stabilizer but a strong $\beta$-stabilizer when in combination with other elements [4]. In conjunction with their bcc phase stabilization effect, these alloying elements are considered to have long term biocompatibility, excellent corrosion resistance, and no allergic reactions [9]. With phase stability playing an important role in the alloy selection for load-bearing implants, a knowledge base of the phase stability in the Ti-Mo-Nb-Ta-Zr system, specifically at low temperatures (<1155 K), is urgently needed. Based on these facts, the thermodynamics and phase stability of the Ti-Mo-Nb-Ta-Zr system were studied in the present work.

The CALPHAD method has been successfully used for the prediction...
of equilibrium phase stabilities and thermodynamic properties of multi-component systems, based on information derived from the pure elements, binary and ternary systems [10–13]. This approach reduces the need for trial-and-error experiments, thus saving time, expenses and other resources [14]. The CALPHAD method incorporates thermochemical data as well as phase equilibria data to build a complete thermodynamic description. In the Ti-Mo-Nb-Ta-Zr system, the binary systems have, at least one if not many, previous thermodynamic descriptions available in the literature. To evaluate the best description to incorporate in the present database, previously published experimental results on the phase equilibria [15–28] and present DFT (Density Functional Theory)-based first-principles calculations on the enthalpy of formation of the bcc phase were used. After the incorporation of the descriptions of all the binary systems, the Ti-containing ternary systems were studied. Of the six Ti-containing ternary systems, Ti-X-Y (X ≠ Y = Mo, Nb, Ta, Zr), three had previous thermodynamic descriptions available in literature that were evaluated for accuracy similarly to the binary systems. Three of the systems, to the best of the authors’ knowledge, had no previous thermodynamic description and thus the necessity of introducing ternary interaction parameters was studied.

This paper is organized as follows. The methodology of the CALPHAD modeling and DFT-based first-principles calculations are outlined in Section 2 including the Vienna Ab-initio Software Package (VASP) input parameters, the special quasirandom structures, and sublattice models. In Section 3 the thermodynamic descriptions of all the binary systems and the modeling of the Ti-containing ternary systems (Ti-Mo-Nb, Ti-Mo-Ta, Ti-Nb-Ta, Ti-Nb-Zr and Ti-Ta-Zr) are presented as well as the first-principles results of the enthalpy of formation of the bcc phase for these systems.

2. Methodology

2.1. CALPHAD modeling

The CALPHAD modeling of the Ti-Mo-Nb-Sn-Ta-Zr system, using the CALPHAD methodology, was built upon the pure elements, binary systems and all the Ti-containing ternary systems for each individual phase [10]. In the present work, the Gibbs energies of formation of pure elements were adopted from the SGTE database [29]. The general model for the molar (m) Gibbs energy of solution phases is expressed by [30]:

$$G_m = \sum x_i G_i^\circ + RT \sum x_i \ln x_i + \sum x_i G_m^\phi$$  \hspace{1cm} (1)

where R is the gas constant, T is temperature. The first term is a summation of the mole fractions of all the elements (x_i) and the molar Gibbs energy of all the pure elements (G_i^\circ) in the specific phase (\phi) being modeled. The second term is the summation of the ideal interactions between all the elements and the last term represents the excess mixing energy, the non-ideal interactions between all the species. The excess mixing energy is expressed by:

$$XSE_m^\phi = \sum_i \sum_{j / i} x_{ij} x_{i} \sum_{\phi} \sum_{y=0} f_{ij}^{\phi}$$

where \(x_{ij}\) is the mole fraction of elements \(i\) and \(j\). The second term is the summation of the interaction parameters between all the elements and the last term represents the excess mixing energy, the non-ideal interactions between all the species.

The interaction parameters are expressed by:

$$\gamma^{\psi}_{ij} \text{ or } \mu^{\psi}_{ij} = a + bT$$  \hspace{1cm} (3)

where \(a\) and \(b\) are model parameters. The interaction parameters may also be represented by an exponential function [31,32].

For the stoichiometric compound, \(A_pB_q\), its Gibbs energy in per mole of unit formula is in the following form in the present work [33]:

$$G_m^{A_pB_q} = a + bT + p^G A_p^\circ + q^G B_q^\circ$$  \hspace{1cm} (4)

where \(a\) and \(b\) are model parameters determined from enthalpy and entropy of formation, \(G_m^\circ\) and \(G_m^\phi\) are the Gibbs energies of pure element \(A\) and \(B\) in their stable element reference (SER) state, i.e. hcp Ti, bcc Mo, bcc Nb, bcc Ta, and hcp Zr, respectively, and \(p\) and \(q\) are the numbers of atoms per unit formula of \(A\) and \(B\), respectively. The evaluations of model parameters in the present work was performed using the PARROT module in the Thermo-Calc software [34].

2.2. First-principles calculations

DFT-based first-principles calculations were used to predict the enthalpy of formation of the bcc phase. The equilibrium properties at 0 K without the contribution of zero-point vibration energy, including equilibrium volume (V_{0b}), energy (E_{0b}), bulk modulus (B) and first derivative of bulk modulus with respect to pressure (\(B'\)), were obtained using an equation of state (EOS) fitting of the energy vs volume (E-V) curve. Here, a four-parameter Birch-Murnaghan EOS equation was used based on the work by Shang et al. [35]

$$E_b(V) = c + dV^{-2/3} + eV^{-4/3} + fV^{-2}$$  \hspace{1cm} (5)

where c, d, e and f are fitting parameters. The enthalpy of formation \(H_{\text{form}}\) of the bcc phase is expressed by:

$$H_{\text{form}} = H_{\text{form}} - (sH_{\text{SER}} + rh_{\text{SER}})$$  \hspace{1cm} (6)

where \(H_{\text{SER}}\) is the enthalpy of a specific structure at composition \(X_Y\), in the bcc phase, \(s\) and \(r\) are the mole fractions of elements \(X\) and \(Y\), respectively. \(H_{\text{SER}}^{\phi}\) and \(H_{\text{SER}}^{\circ}\) are the molar enthalpies of the pure elements \(X\) and \(Y\) in their SER state, respectively. For each binary system, 3 special quasirandom structures at different compositions, discussed below, were used as well as at least 2 more dilute structures at different compositions, i.e. Ti-Mo 4 dilute structures (Mo_{33}Ti 54-atoms, Mo_{55}Ti 16-atoms, Ti_{53}Mo 16-atoms), Ti-Nb 4 dilute structures (Nb_{55}Ti 54-atoms, Nb_{55}Ti 16-atoms, Ti_{53}Nb 54-atoms, Ti_{53}Nb 16-atoms), Ti-Ta 5 dilute structures (Ta_{55}Ti 54-atoms, Ta_{55}Ti 16-atoms, Ti_{53}Ta 16-atoms, Ti_{53}Ta 54-atoms, Ti_{53}Ta 16-atoms, Ti_{53}Ta 54-atoms). A different number of dilute structures were done based on the complexity of some of the structures being unstable. For the Ti-X-Y (X ≠ Y = Mo, Nb, Ta, Zr) ternary systems, SQS structure calculations were completed at three compositions as discussed below.

SOS are small supercells used to mimic randomly substituted structures in terms of correlation functions but reduce the error associated with calculating actually randomly substituted structures [36]. For the Ti-X binary systems, the SOS’s were each 16-atom supercells of Ti_{15}X_{16}, Ti_{16}X_{15}, and Ti_{17}X_{14} compositions, respectively, developed by [37]. For the Ti-X-Y ternaries, the SOS’s were Ti_{15}X_{15}Y_{12} (36-atom), Ti_{16}X_{16}Y_{16} (64-atom) compositions, respectively, developed by Jiang et al. [37,38]. In order to be able to effectively visualize the DFT-based first-principles results for the Ti-X-Y systems versus the modeling the plots went from a 50–50 binary mixture of the alloying elements to pure Ti. For this graph, results from DFT-based first-principles calculations for the binary SOS structure (X_{16}Y_{16} 16-atom, X ≠ Y = Mo, Nb, Ta, Zr) were first obtained. The relaxation of these SOS structures is complicated because local atomic relaxations far from the original bcc lattice can cause the structure to lose the bcc lattice symmetry. To preserve symmetry, the calculations were carried out with three different relaxation schemes: 1) only the cell volume is relaxed 2) the cell volume and shape are relaxed simultaneously and finally 3) the cell volume, shape, and ionic positions are simultaneously relaxed. The relaxed structure with the lowest energy that preserved the bcc symmetry was used and the relaxation scheme that lead to this structure is shown in the supplementary. To verify whether the SOS keeps the bcc lattice symmetry after the relaxation, codes that are available in VASP [39] and phonopy [40] were used to check the symmetry of the...
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