

Full length article

Evaluation of the tantalum-titanium phase diagram from *ab-initio* calculations

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ABSTRACT

The thermodynamic properties of the Ta-Ti binary system below 900 °C are not well known. In particular, the location and shape of the *solvus* between the phase separation region at low temperatures and the solid solution at high temperatures are not well defined. In this study, we present a thermodynamic description for this system based on *ab-initio* calculations. The formation enthalpies of bcc and hcp solid solutions are estimated using the special quasi-random structures methodology and their vibrational free energy calculated by the quasi-harmonic Debye model. The excess energies of the solid solutions are fitted to a sub-subregular model and used to define the phase diagram of the binary system. It is shown that the current empirical assessment of the energies of the pure elements leads to a phase diagram that strongly departs from the known experimental features at low temperatures. An *ab-initio* guided correction of these energies is necessary to obtain correctly the low temperature phase separation and the high temperature solid solution. The predicted *solvus* of the phase diagram is qualitatively different from those previously reported for the Ta-Ti system. It exhibits a miscibility gap between two distinct bcc phases, similar to those that exist in the closely related binary systems Ta-Zr, Ta-Hf, Cr-Ti, Mo-Ti, V-Ti, and Ti-W.

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1. Introduction

The demand for materials suitable for permanent implants in the human body grows as people live longer and their bones weaken with age. Ta-Ti alloys have been proposed as one of the best choices for biomedical applications based on their excellent biocompatibility in the human body environment, high strength, relatively low elastic moduli and enhanced corrosion resistance [1–6]. These alloys are also attractive for applications in advanced actuators since they exhibit shape memory behavior at relatively high temperatures due to a reversible martensitic transformation between the meta-stable bcc phase and the α martensite phase [7–13]. Despite the potential applications of these alloys, important gaps exist in our knowledge of their binary phase diagram. The phase diagram has been studied experimentally [14–17] and modeled using the computational thermodynamics CALPHAD approach [18–20]. In these studies, no inter-metallic compounds

were observed in the Ta-Ti system. At temperatures higher than 400–900 °C, depending on the composition, the stable phase is a single bcc solid solution that decomposes into the elemental hcp and bcc structures at lower temperatures. Fig. 1 shows a schematic Ta-Ti phase diagram assessed from the latest thermodynamic data [20].

Some controversy exists as to the exact location of the *solvus* [15–18]. The various reports on the *locus* of the *solvus* were discussed by Murray [21], who suggested that the variation was probably due to contaminations or inadequate experimental quench rates. Knowledge of the accurate location of the *solvus* is necessary for the design of thermal treatments for control and tailoring of the properties of Ta-Ti alloys.

To the best of our knowledge there are no published *ab-initio* studies to compute the Ta-Ti phase diagram. In this study we utilize density functional theory (DFT) to study this system at temperatures below 900 °C. We employ the AFLOW high-throughput framework [22] to screen a database of ordered structures and estimate the formation enthalpies of bcc and hcp solid solutions using the special quasi-random structures (SQS) methodology [23]. The ideal expression for the configuration entropy and the quasi-

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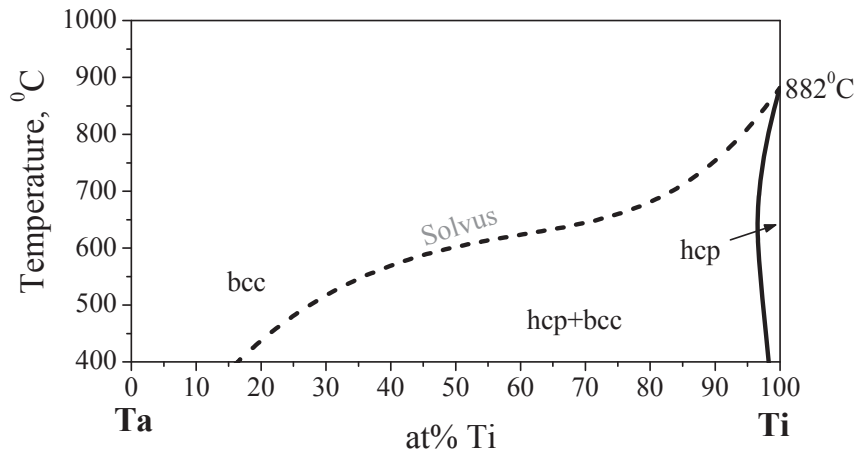


Fig. 1. Schematic Ta-Ti phase diagram assessed from experimental data [20].

harmonic Debye model for the vibrational energy are used to estimate the finite temperature contributions to the free energy. This analysis of the alloys' free energy leads to a binary phase diagram that is qualitatively different from those previously reported for the Ta-Ti system. It exhibits a wide phase separation hump on the *solvus* between two distinct bcc phases, similar to those that appear in the closely related binary systems Ta-Zr, Ta-Hf, Ti-Cr, Ti-Mo and Ti-W [24]. It thus improves our thermodynamic understanding of the system and provides a more solid basis for both fundamental and applied research into Ta-Ti alloys. In particular, this understanding should assist the development of better thermal treatments for applications of Ta-Ti products.

2. Methodology

2.1. DFT calculations

To investigate the Ta-Ti phase diagram we utilized *ab-initio* electronic structure calculations within the framework of density functional theory (DFT). We start by screening an extensive database of ordered stoichiometric structures via the high-throughput framework AFLOW [22]. In addition, the pure elements in the hcp and bcc structures and SQS on the bcc and hcp lattices, at compositions $\text{Ta}_{0.75}\text{Ti}_{0.25}$, $\text{Ta}_{0.5}\text{Ti}_{0.5}$ and $\text{Ta}_{0.25}\text{Ti}_{0.75}$, are calculated to estimate the formation energies of the corresponding solid solutions. For these calculations, we used the 16-atoms per unit cell structures reported in Refs. [25,26] for the bcc- and hcp-SQS, respectively. All total energy calculations were carried out employing the VASP software [27] within the AFLOW standard for material structure calculations [22,28]. We used projector augmented waves (PAW) pseudopotentials [29] and the exchange correlation functionals parameterized by Perdew, Burke, and Ernzerhof (PBE) [30] for the generalized gradient approximation (GGA). The energies were calculated at zero temperature and pressure, with spin polarization and without zero-point motion or lattice vibrations. All crystal structures were fully relaxed (cell volume and shape and the basis atom coordinates inside the cell). Numerical convergence to about 1 meV/atom was ensured by a high-energy cutoff, 30% higher than the highest energy cutoff for the pseudopotentials of the components, and dense 6000 k-point per reciprocal atom Monkhorst-Pack meshes [31]. Complete information about the over 200 ordered structures calculated for the Ta-Ti system, including initial and relaxed structures and detailed calculation specifications, can be obtained in the open access AFLOWLIB materials data repository [32,33].

It should be noted that, under full relaxation, the hcp-SQS $\text{Ta}_{0.75}\text{Ti}_{0.25}$ and $\text{Ta}_{0.5}\text{Ti}_{0.5}$ changed their geometry and relaxed into the corresponding bcc-SQS. This is in qualitative agreement with the experimental phase diagram of Ta-Ti alloys (Fig. 1), where instability of the hcp solid solution should be expected at high Ta concentrations. Therefore, for these structures, we also performed a series of partial relaxations, volume relaxation followed by either shape relaxation for the unit cell and atomic minimization for the location of the atoms in this unit cell or vice versa. The properties of the hcp solid solution at these concentrations are hereafter estimated using the results of these restricted calculations, selecting the lowest energy obtained by a structure that preserved the hcp symmetry under partial relaxations. For the $\text{Ta}_{0.75}\text{Ti}_{0.25}$ hcp-SQS this lowest energy is obtained by a volume relaxation followed by a relaxation of atomic positions without shape relaxation. For the $\text{Ta}_{0.5}\text{Ti}_{0.5}$ it is obtained by a volume relaxation followed by consecutive but separate atom positions and shape relaxations.

The calculations of the total energies of the relaxed hcp- and bcc-SQS were repeated using a full potential method, employing the Augmented Plane Waves + local orbitals (APW + lo) formalism as implemented in the WIEN2k code [34,35]. In these calculations the core states treatment is fully relativistic [36] and the valence states are considered in the scalar relativistic approximation [37]. The GGA-PBE exchange correlation potential was employed, as in the VASP calculations. The radii of the muffin-tin spheres (R_{mt}) were 2.3 a.u. for both Ti and Ta. It was found that a basis-set size of $R_{\text{mt}}K_{\text{max}} = 11$ and a k -mesh of 600 points for the SQS and 3500 points for the pure elements suffices to reach an accuracy of $\sim 10^{-4}$ Ry in the total-energy calculations, with an energy cutoff separating core and valence states of -6 Ry. Here K_{max} represents the magnitude of the largest K vector in the wave function expansion. Partial structure relaxation was carried out by optimization of the lattice parameters and minimization of the internal location of the atoms in the cell as described in Refs. [38,39].

2.2. Thermodynamic modeling

The formation enthalpy of a binary intermetallic structure is given by

$$H^f(\text{Ta}_{(1-x)}\text{Ti}_x) = H(\text{Ta}_{(1-x)}\text{Ti}_x) - (1-x)H(\text{Ta}) - xH(\text{Ti}) \quad (1)$$

where $H(\text{Ta}_{(1-x)}\text{Ti}_x)$ is the enthalpy per atom of the intermetallic structure and $H(\text{Ta})$ and $H(\text{Ti})$ are the enthalpies per atom of the

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