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The effect of lattice stability determination on the computational phase diagrams of intermetallic alloys

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ABSTRACT

The evaluation of lattice stabilities of unstable elemental phases is a long-standing problem in the computational assessment of phase diagrams. Here we tackle this problem by explicitly calculating phase diagrams of intermetallic systems where its effect should be most conspicuous, binary systems of titanium with bcc transition metals. Two types of phase diagrams are constructed: one based on the lattice stabilities extracted from empirical data, and the other using the lattice stabilities computed from first principles. It is shown that the phase diagrams obtained using the empirical values contain clear contradictions with the experimental phase diagrams at the well known limits of low or high temperatures. Realistic phase diagrams, with a good agreement with the experimental observations, are achieved only when the computed lattice stability values are used. At intermediate temperatures, the computed phase diagrams resolve the controversy regarding the shape of the solvus in these systems, predicting a complex structure with a eutectoid transition and a miscibility gap between two bcc phases.

1. Introduction

The systematic experimental inspection of thermodynamic properties of alloys is usually based on phenomenological rules and metallurgical experience. It requires considerable efforts commonly associated with melting, casting, heat treatments, homogenization and characterization of series of alloys, which set practical limits on its applicability to a relatively small part of the potential alloy space. Theoretical inspection based on a bottom-up design strategy may enhance the experimental approach, and ultimately replace most of it, by providing rapid computational predictions of structural and thermodynamic properties. The bottom-up strategy becomes viable with the advent of powerful computational methods and available resources. Moreover, the theoretical approach brings a better understanding of alloy design and can reveal shortcuts to achieve the desired alloys as opposed to the trial and error methods used in conventional metallurgical screening.

In this work we investigate the binary systems of titanium with the bcc transition metals Mo, Nb, Ta and V. These systems are prominent examples of β-Ti alloys, where the temperature range of the bcc solid solutions is significantly extended by mixing titanium with a β-stabilizing element. Such titanium alloys are important in an enormous range of applications including aerospace and marine technology, where strength, low weight, and resistance to corrosion and high temperatures are important; biological implants, e.g. artificial hips and pins for setting bones, since they do not react within the human body; and additional specialty applications, e.g. sports equipment (golf clubs, etc.) and shape memory alloys [1,2]. A wide variety of metallurgical processes, heat treatments and aging, are applied to optimize special properties, such as fracture toughness, fatigue strength and high temperature creep strength, and to tailor the alloys for specific applications. The improvement of such processes and the development of new ones for an even wider range of future applications requires intimate understanding of the phase diagrams of these alloy systems.

The fundamental quantity expressing the thermodynamic stability of alloys is the free energy. The phase diagram of an alloy system is determined by evaluating the Gibbs free energy difference between its relevant phases, either ordered or disordered. The free energy of a solid solution phase, ϕ, in a binary system is expressed by

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$$G^{\phi}(x_{\mathrm{A}},x_{\mathrm{B}},T) \quad = \quad x_{\mathrm{A}}\cdot{}^{0}G_{\mathrm{A}}^{\phi}(T)+x_{\mathrm{B}}\cdot{}^{0}G_{\mathrm{B}}^{\phi}(T)+{}^{\mathrm{mix}}G^{\phi}(x_{\mathrm{A}},x_{\mathrm{B}},T)+{}^{\mathrm{ex}}G^{\phi}(x_{\mathrm{A}},x_{\mathrm{B}},T), \tag{1}$$

where ${}^{0}G_{\mathrm{A}}^{\phi}$ and ${}^{0}G_{\mathrm{B}}^{\phi}$ are the Gibbs energies of the pure elements A and B in the ϕ structure, T is the absolute temperature, ${}^{\mathrm{mix}}G^{\phi}$ is the mixing energy of the ideal solution

$${}^{\mathrm{mix}}G^{\phi}(x_{\mathrm{A}},x_{\mathrm{B}},T)=k_{\mathrm{B}}T(x_{\mathrm{A}}\log x_{\mathrm{A}}+x_{\mathrm{B}}\log x_{\mathrm{B}}) \tag{2}$$

and ${}^{\mathrm{ex}}G^{\phi}$ is the excess energy that represents the effects of non-ideality

$${}^{\mathrm{ex}}G^{\phi}={}^{\mathrm{ex}}H^{\phi}+{}^{\mathrm{ex}}G_{\mathrm{vib}}^{\phi} \tag{3}$$

with the excess enthalpy

$${}^{\mathrm{ex}}H^{\phi}=H_{\mathrm{AB}}^{\phi}-x_{\mathrm{A}}\cdot H_{\mathrm{A}}^{\phi}-x_{\mathrm{B}}\cdot H_{\mathrm{B}}^{\phi} \tag{4}$$

and the excess vibrational energy

$${}^{\mathrm{ex}}G_{\mathrm{vib}}^{\phi}=G_{\mathrm{vib,AB}}^{\phi}-x_{\mathrm{A}}\cdot G_{\mathrm{vib,A}}^{\phi}-x_{B}\cdot G_{\mathrm{vib,B}}^{\phi}. \tag{5}$$

The excess energy is often not available directly from simple experiments, and obtaining it requires considerable effort. It, therefore, usually has to be evaluated computationally. The Gibbs energy difference between the equilibrium and unstable phases of a single element is called *lattice stability*. This quantity is a crucial component in the construction of computational phase diagrams involving elements belonging to different lattice systems, e.g. an hcp-element and a bcc-element. In particular, it presents a conceptual problem in cases where one element is mechanically unstable at low-temperatures in the structure of the other, since the physical meaning of the computed lattice stability is then unclear. This problem has attracted much discussion in the literature, but has yet to be settled [3–11]. It currently presents a major impediment to the development of computational phase diagram databases.

Empirical estimations of lattice stabilities were developed by the Scientific Group Thermodata Europe (SGTE) [12] by direct measurements on pure elements in their stable structures and extrapolations of activity measurements of alloys for the unstable structures. Alternatively, the lattice stability of the pure elements can be easily computed by *ab-initio* methods. Wang et al. [6] found a good agreement for the lattice stability between the computed and the empirical estimations for non-transition elements. In these cases, only small differences up to 15 meV/atom were found. However, large discrepancies, most of them in the range of 80–300 meV/atom, were found for the transition metals [4,7].

Here, we consider these two approaches for assessing lattice stabilities, one empirical and the other computational, aiming to reveal the appropriate approach for constructing the binary phase diagrams of mixed bcc-hcp transition metal systems. We chose four binary systems of the hcp-element titanium, which is well known to be unstable in the bcc phase at low temperatures, where a bcc solid solution is a prominent feature at higher temperatures over the entire range of compositions. The empirical approach is based on the energies cited in the SGTE database [12]. In the computational approach, these SGTE values are adjusted to reproduce the lattice stabilities computed *ab-initio* for the two elements. These two sets of lattice stabilities are used to construct two sets of TM-Ti (TM = Nb, Mo, V, Ta) binary phase diagrams and thus demonstrate that the development of computational phase diagrams, of mixed lattice intermetallic alloy systems, requires *ab-initio* based evaluation of the lattice stabilities of their components.

2. Ab initio modeling

We start the investigation of the binary phase diagrams by an *ab-initio* screening of ordered stoichiometric structures via the high-throughput framework AFLOW [13–15] and calculate their formation enthalpies

$$H_F\left(\mathrm{TM}_{(1-x)}\mathrm{Ti}_x\right)=H\left(\mathrm{TM}_{(1-x)}\mathrm{Ti}_x\right)-(1-x)H(\mathrm{TM})-xH(\mathrm{Ti}) \tag{6}$$

where $H\left(\mathrm{TM}_{(1-x)}\mathrm{Ti}_x\right)$ is the enthalpy per atom of the intermetallic structure and $H(\mathrm{TM})$ and $H(\mathrm{Ti})$ are the enthalpies per atom of the elements at their ground state structures, bcc-TM and hcp-Ti. Negative formation enthalpies signify structures that are energetically favorable compared to phase separation into the elemental structures and are therefore possible candidates for stable compounds in the binary system. In addition, the special quasirandom structures (SQS) for the bcc [16] and hcp [17] structures were computed to estimate the excess enthalpies of the corresponding solid solutions.

Total energy calculations were carried out employing the VASP software [18] within the AFLOW standard for material structure calculations [19]. We used projector augmented waves (PAW) pseudopotentials and the exchange correlation functionals parameterized by Perdew, Burke, and Ernzerhof (PBE) 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.

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 plus local orbitals (APW + lo) formalism as implemented in the WIEN2k code [20,21]. In these calculations the core states treatment is fully relativistic and the valence states are considered in the scalar relativistic approximation. The GGA-PBE exchange correlation potential was employed, as in the VASP calculations. A muffin-tin sphere $R_{\mathrm{mt}}=2.3$ a.u., a basis-set size of $R_{\mathrm{mt}}K_{\mathrm{max}}=11$ and a **k**-mesh of 600 points for the SQS and 3500 points for the pure elements were used to reach an accuracy of 10^{-4} Ry, with an energy cutoff separating core and valence states of -6 Ry.

The contribution to the Gibbs energy at elevated temperatures, i.e. the vibrational free energy, was considered according to the GIBBS methodology [22,23] in the quasiharmonic Debye model. The electronic and magnetic excess contributions to the Gibbs energy are expected to be much smaller in these systems and are therefore neglected. The computed excess energies for the two