

Influence of stresses on structure and properties of Ti and Zr-based alloys from first-principles simulations

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Abstract. Computer simulations in the framework of the Density Functional Theory have become an established tool for computer simulations of materials properties. In most cases, however, information is obtained at ambient conditions, preventing design of materials for applications at extreme conditions. In this work we employ *ab initio* calculations to investigate the influence of stresses on structure and stability of Ti-Mo and Zr-Nb alloys, an important class of construction materials. Calculations reproduce known phase stability trends in these systems, and we resolve the controversy regarding the stability of body-centered cubic solid solution in Mo-rich Ti-Mo alloys against the isostructural decomposition. Calculated results are explained in terms of the electronic structure effects, as well as in terms of physically transparent thermodynamic arguments that relate phase stability to deviations of concentration dependence of atomic volume from the linear behavior.

1. Introduction

Growing economy constantly requires new materials, and about 150 years ago their discoveries accelerated substantially. The success is associated with increasing information technology contents in new materials. Novel phases are continuously synthesized, and the challenge is to identify potentially significant materials, to develop efficient technological processes, and to optimize their functionality. Emergence of new and powerful instruments such as computers initiated further development of computer modeling as a qualitatively new branch of science. The major goal of the theory in applications within the materials sciences is to assist experimentalists and engineers in a design of new materials and to discover phenomena with high potential to improve the existing products, as well as to create qualitatively new products.

One of the most impressive developments within the theoretical simulations of materials properties during the last four decades is associated with an approach of a new field, *ab initio* computer simulations based on the electronic structure theory [1]. Within this method simulations are carried out on the basis of the most fundamental laws of physics, e.g. quantum mechanics, statistical physics, theory of elasticity, and in principal without any experimental input. Accelerated by a revolutionary progress in computer technologies, the electronic structure theory has become a mature field of the



modern science. Computers rapidly became an essential and integrated part of materials design. Already at present one can witness a gradual substitution of a traditional trial-and-error approach by a knowledge-based materials design. Nowadays, computer simulations, experiment, and theory contribute on equal footing to the accumulation of new knowledge, to accessing and assembling materials parameters, and to establishing novel design concepts.

Unfortunately, most of the simulations reported in the literature are carried out at ambient conditions. Moreover, most applications of thermodynamic databases to materials design are limited to ambient pressure. Thus, the consideration of elastic contributions to thermodynamic stability is highly desirable, but not straight-forward to realise [2]. Moreover, a complexity of the problem increases substantially with increasing complexity of materials when, in addition to the pressure one varies their chemical composition. On the other hand, an ability to understand and a possibility to predict a response of a physical system upon a variation of external parameters is one of the core tasks for theoretical simulations.

The goal of this work is to investigate, by means of state-of-the-art tools for *ab initio* calculations, the influence of stresses on structure and stability of Ti and Zr-based alloys. Ti alloys are important, e.g. for aerospace and medical applications. However, hcp Ti alloys do not have high strength, though they show strong hardening during cold deformation. Their disadvantage is reduced technological plasticity. Thus, there is increasing interest in bcc Ti alloys. Mo, among few other elements, is known as bcc-Ti stabilizer. Zr-based alloys represent a material system widely used in nuclear energy applications, e.g. as fuel cladding materials. Requirements to increase fuel efficiency and to reduce the amount and activity of nuclear waste are directly related to the need to improve the properties of zirconium alloys, including their resource characteristics: durability, fatigue strength and corrosion resistance. In this work the results of our *ab initio* study of mixing enthalpies and lattice stabilities for binary Ti-Mo and Zr-Nb alloys are reported and general understanding of modifications of these properties upon application of high pressure are established.

2. Theoretical methodology

Materials properties and their performance in applications are determined by chemical composition, temperature, and pressure. Their variation can give rise to phase transitions, e.g. associated with the change of the underlying crystal structure, for instance from hexagonal closed packed (hcp) to body centred cubic (bcc) or with a modification of distributions of the alloy components on the lattice sites on the same underlying lattice, like an isostructural spinodal decomposition [3]. These two effects will be in focus for the present study.

2.1. General considerations

A phenomenological theory of phase transitions follows from equilibrium thermodynamics. However, it is important to notice that while experimentally the phase equilibria are most often studied at constant pressure conditions, the first-principles calculations are most often done at constant volume. In the former case the equilibrium is described by the Gibbs free energy:

$$G = E + PV - TS, \quad (1)$$

where E is the energy of the system, S denotes the entropy, and thermodynamic variables P , V , T represent pressure, volume, and temperature, respectively. General conditions for equilibrium are represented by G minimum. Within the *ab initio* approach one considers most often conditions corresponding to fixed parameters T and V , and the equilibrium is described by the Helmholtz free energy:

$$F = E - TS. \quad (2)$$

Comparing equations (1) and (2), we see that the PV term is most often left off the theory.

A justification for this approach comes from the fact that for equilibria involving only solid and liquid phases, the phase boundaries are typically shifted only by the order of a few hundredths of a degree per bar change in P , and therefore the effect of PV -term upon the phase transitions temperature is often assumed to be negligible [4]. However, the rapid advances of modern technology as well as developments in high-pressure experiments invalidate the above argument. For instance, in modern cutting tools applications the force against the work piece, together with the minimal contact area, gives rise to stress or pressure levels of few GPa [5]. Such extreme compressions may affect structure and stability of construction materials.

To elucidate the effect of uniform stress or pressure on the structure and phase stability of Ti and Zr-based alloys, the temperature effects are neglected, thus putting the last term in the right-hand side of equations (1) and (2) to zero, and focus on the calculation of the enthalpy:

$$H = E + PV. \quad (3)$$

The lattice stability of phase α with respect to phase β is therefore defined by the entropy difference $H_\alpha - H_\beta$ at fixed composition, and its negative value corresponds to a stability of the phase α . On the other hand, a stability of the alloy with respect to its decomposition into pure components is given by the enthalpy of mixing:

$$\Delta H_{A_{1-x}B_x}^{mix} = H_{A_{1-x}B_x} - (1-x)H_A - xH_B, \quad (4)$$

where $H_{A(B)}$ is the enthalpy of the alloy pure components. In the following the isostructural mixing enthalpy is distinguish from the total one. In the former case the pure components are simulated in the same crystal structure as the alloy. In the latter case they are considered in their respective lowest energy a state that is in the ground states. The isostructural mixing enthalpy characterizes the tendency towards alloying (negative values) or segregation (positive values) at the fixed crystal lattice. It is important, e.g. for mutiscale modeling [3]. The total mixing enthalpy characterizes phase stability more directly, because it includes both, the effects of the lattice stability and the mixing.

2.2. Computational techniques

The calculations of the total energy E in equation (3) were performed in the framework of the Density Functional Theory (DFT) [1] using the exact muffin-tin orbital (EMTO) method combined with the coherent potential approximation (CPA) for the electronic structure of random alloys [6]. The self-consistent electron densities were obtained within the Generalized Gradient Approximation (GGA) [1] using full charge density formalism [6]. The applicability of DFT and EMTO for the pure alloy components has been demonstrated recently in [7], while CPA has been successfully applied for calculations of lattice parameters and bulk moduli of Zr-Nb and Ti-Al-Mo-V alloy in [8].

The energy integration has been carried out in the complex plane using a semi-elliptic contour comprising 24 energy points. The calculations were performed for a basis set including valence s, p, d , and f orbitals, whereas the core states were recalculated at each iteration of the self-consistency loop. The integration over the irreducible part of the Brillouin zone was performed using a $29 \times 29 \times 29$ grid of k -points in the reciprocal space for bcc and face centred cubic (fcc) lattices. For the hcp it is used $21 \times 21 \times 17$ grids of k -points. The convergence of the energy with respect to the calculation parameters was 10^{-8} Ry.

The equation of state (EOS) was determined by calculating the total energy of the alloy $E(V_{at})$ for a set of volumes (per atom) V_{at} . In this work $E(V_{at})$ dependence was fitted by the modified Morse function [9]. Note that for hcp crystals the ratio of the lattice constants c/a for each volume V_{at} is optimized by minimizing the energy $E(V_{at}, c/a)$ with respect to c/a . The equations of state are constructed with the help of the so-obtained minima of the function $E(V_{at}, c/a)$. The pressure in equation (3) was calculated as $P(V_{at}) = -\partial E(V_{at}) / \partial V_{at}$ by analytical differentiation of the Morse function. The accuracy of the calculated EOS for the pure components using the computational tools employed in this work has been demonstrated in [7].

3. Results

Calculated total mixing enthalpies for bcc, fcc and hcp Mo-Ti and Nb-Zr alloys at two values of pressure, 0 GPa and P=10 GPa are shown in Figures 1 and 2, respectively. At first the reliability of these results is analyzed. The main tool for the experimental determination of the mixing enthalpy, the calorimetry, is getting rare, probably due to its relatively high cost. In particular, the authors could not find any experimental information for the two systems considered in this work. This underlines the importance of theoretical simulations. General accuracy of the adopted theoretical scheme is well established in the literature [3,5,6].

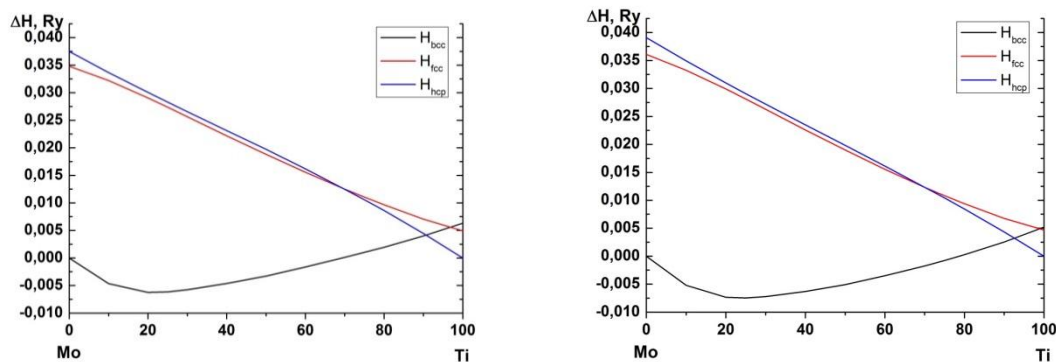


Figure 1. Calculated total mixing enthalpies for bcc (black lines), fcc (red lines) and hcp (blue lines) Mo-Ti alloys at P=0 GPa (left panel) and P=10 GPa (right panel) as a function of Ti concentration (in at. %).

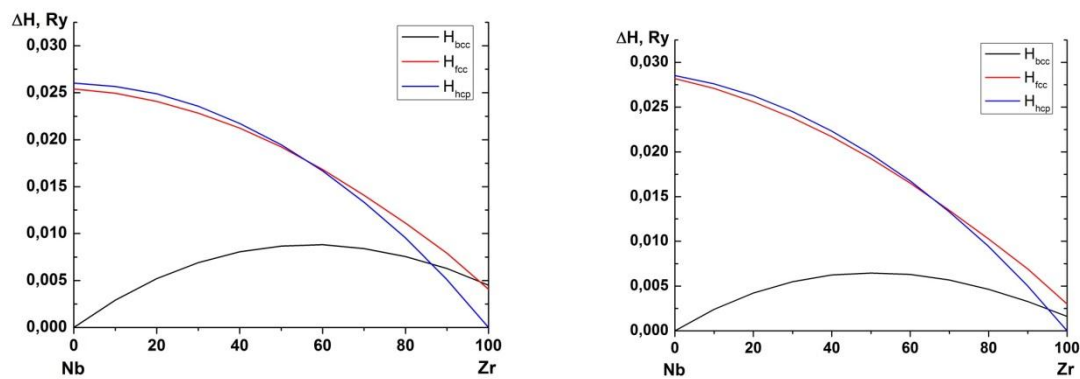


Figure 2. Calculated total mixing enthalpies for bcc (black lines), fcc (red lines) and hcp (blue lines) Nb-Zr alloys at P=0 GPa (left panel) and P=10 GPa (right panel) as a function of Zr concentration (in at. %).

Calculations reproduce known experimental trends in the two systems. Indeed, fcc alloys are neither stabilized in these two systems, in agreement with experiment. Therefore it is not discussed in the remaining part of this paper. At low temperature Nb-Zr system is characterized by a tendency towards phase separation into hcp Zr-rich and bcc Nb-rich phases, in complete agreement with the behavior of the mixing enthalpy shown in Figure 2. Next, in the calculations the enthalpy difference between bcc and hcp Mo-Ti alloys decreases rapidly when Mo is added to Ti (Figure 1). This is also in agreement with experiment, as Mo is known as β -Ti stabilizer (it stabilizes the bcc phase). Experimental situation on the stability of bcc solid solution in alloys with higher fraction of Mo in this system is somewhat more controversial. From the one hand, there are experimental studies that claim the presence of isostructural decomposition in bcc Mo-Ti system, in addition to the decomposition into bcc Mo-rich

and hcp Ti-rich phases. On the other hand, SGTE and NIST phase diagrams claim the stability of the bcc Mo-rich solid solution. The isostructural mixing enthalpy of bcc Mo-Ti alloys is shown in Figure 3. It is negative in the whole interval of concentrations, indicating the stability of the solid solutions and supporting SGTE and NIST phase diagrams. Thus, the calculated results give reliable trends for the mixing enthalpies in Mo-Ti and Nb-Zr systems. At the same time, the absolute values should be taken with some care because of the neglect of the contribution from the local distortions of the crystal lattice in the CPA [3]. Moreover, recently it has been demonstrated that bcc phases of Zr and Ti are strongly anharmonic [10,11]. Therefore, one may expect an influence of temperature on the calculated properties of these alloys. However, neither of these effects should influence the calculated trends, which are discussed in the next section.

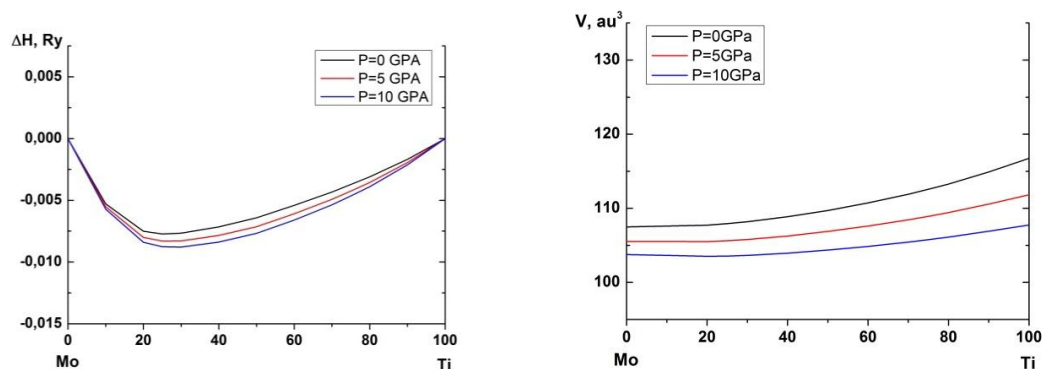


Figure 3. Calculated isostructural mixing enthalpies (left panel) and volume per atom V (right panel) for bcc Mo-Ti alloys at $P=0$ (black lines), 5 GPa (red lines) and 10 GPa (blue lines) as a function of Ti concentration (in at. %).

4. Discussion

Discussing the influence of pressure on the phase stability in the considered systems, in Mo-Ti system the bcc phase is getting more favourable energetically with respect to the hcp phase at about 10 at. % of Mo at ambient pressure. At 10 GPa the crossover occurs at even smaller concentration of 5 at. % Mo (Figure 1). The similar effect is seen in Nb-Zr system, that is both, the pressure and alloying with Nb stabilize the bcc phase with respect to the hcp one (Figure 2). Indeed, the line corresponding to calculated total mixing enthalpy for the bcc phase crosses the one for the hcp phase at ~ 12 at. % of Nb in Zr at ambient pressure, while the crossing occurs at ~ 5 at% at $P=10$ GPa.

The observed stabilization of the bcc phase can be explained by the electronic structure effects in the framework of the so-called canonical d -band model [12]. According to it the energy difference among different closed-packed crystal structures can be determined from a sum of one-electron, or band energies up to the highest occupied electronic level, the so-called Fermi energy. For transition metals the Fermi energy is defined by the number of d -electrons, and therefore the lattice stability can be written as a function of the occupation of the d -band [12]. The canonical band theory allows us to explain trends of the lattice stability upon the change of the band filling due to alloying of Ti and Zr with Mo and Nb, respectively. Isoelectronic elements, Ti and Zr, belong to the stability field of the hcp crystal structure. But both of them are close to the hcp-bcc boundary, and increasing their d -band filling by adding more electrons into the system should stabilize the bcc phase. Alloying with Nb/Mo increases the number of electrons because they have more d -electrons than Ti/Zr. Pressure increases the occupation of the d -band due to s - to d -charge transfer mechanism. Thus, both, pressure and alloying should stabilize the bcc phases in these systems, in agreement with our *ab initio* calculations.

Considering the effect of the uniform stress on the stability of solid solution phases against isostructural decomposition, one sees in Figure 3 that pressure decreases the mixing enthalpy, thus making the alloy more stable. This effect can be explained from the model proposed by Alling *et al.* in

[5]. Using the thermodynamic relations between the pressure derivative of the Gibbs free energy and volume per atom, Alling *et al.* showed that negative deviations of the concentration dependence of the latter should lead to more negative values of the former. In the right panel of Figure 3 we show calculated concentration dependence of the volume per atom in Mo-Ti alloys, which clearly have negative deviations from the linear concentration dependence. Thus, the predicted pressure-induced stabilization of bcc solid solutions in Mo-Ti alloys is in agreement with Alling's model.

5. Conclusion

The influence of stresses on structure and stability of Ti and Zr-based alloys have been investigated by means of state-of-the-art *ab initio* simulations. The exact muffin-tin orbital method combined with the coherent potential approximation was used for calculations of the electronic structure and total energy of random Mo-Ti and Nb-Zr alloys. The results observed that the application of the uniform stress and alloying with Mo/Nb stabilize bcc phases of Ti/Zr-based alloys relative to the hcp phase. In Ti-Mo system the pressure also increases the stability of the bcc solid solution against the isostructural decomposition. The observation is explained by the filling of Ti and Zr *d*-band by electrons upon the alloying and compression. In addition, our calculations provide support to a thermodynamic model of Alling *et al.* [5] that relates the pressure dependence of the stability of solid solutions to deviations of atomic volumes in alloys from linear concentration dependence.

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