Mixing enthalpies of alloys with dynamical instability: bcc Ti-V system

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Skripnyak, N., Ponomareva, A. V., Belov, M. P., Syutkin, E. A., Khvan, A. V., Dinsdale, A. T., Abrikosov, I. A., (2020), Mixing enthalpies of alloys with dynamical instability: bcc Ti-V system, *Acta Materialia*, 188, 145-154. <https://doi.org/10.1016/j.actamat.2020.01.056>

Original publication available at:

<https://doi.org/10.1016/j.actamat.2020.01.056>

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Abstract

Enthalpy of mixing is among the key materials parameters to determine phase stability and phase transformations in solid solutions. The possibility to predict it from first principles in the framework of the density functional theory is one of the corner stones of the modern materials modeling and the future data-driven materials design. Here we have considered body-centered cubic (bcc) Ti-V alloys, a system with high potential for aerospace, automotive biomedical and energy applications, which is known to exhibit the dynamical instability of the crystal lattice for Ti-rich alloys at low temperature. We have calculated the mixing enthalpies ΔH of bcc Ti-V alloys in the whole interval of concentration at high temperature using *ab initio* molecular dynamics (AIMD) simulations. A comparison with state-of-the-art static calculations at temperature 0K shows drastic difference between the two methods: while AIMD predicts positive values of ΔH in the whole range of concentrations, the static zero-temperature simulations result in negative values of ΔH for Ti-rich alloys. We have measured the mixing enthalpy of bcc Ti-V alloys experimentally at 1073 K using an isoperibol high temperature Tian-Calvet calorimeter and found that the enthalpies are positive, in agreement with our finite temperature AIMD calculations. We attribute the failure of the standard static calculations of ΔH to lattice distortions associated with the dynamical instability of bcc Ti-V alloys at zero temperature and argue that the effect should be generally important in theoretical predictions of thermodynamic properties, especially for systems with dynamical instability.

Keywords: Ti-V alloys, thermodynamic properties, *ab initio*, molecular dynamics, enthalpy of mixing, calorimetry

1. Introduction

One of the challenging tasks of the modern condensed matter theory is to predict key materials properties. A relevant problem consists of replacing, at least partially, the labor-intensive and costly full-scale experimental studies of promising materials by their theoretical modeling. *Ab initio* or first-principles methods serve as a powerful tool for generation of reliable data on thermodynamic properties. It is clear, however, that quantum mechanics cannot be used in isolation because of time and length scale limitations. Therefore, multiscale modeling using parameters determined from quantum mechanics appears as a promising way for moving forward such research. At present, various methods of multiscale modeling are used; they help to solve macro-scale problems by considering the effects at different levels for large systems and for long simulation times. However, higher-level simulations within the multiscale modeling scheme require input parameters. More and more often such parameters are provided by the first-principles calculations. Moreover, large databases of computed parameters are under construction, and the data is believed to be important for the knowledge-based design of advanced materials, e.g. via multiscale modeling or novel approaches like machine learning, data mining and artificial intelligence [1-3]. Quality and reliability of the assembled data plays the most important role in the advancement of the data-driven materials design.

State-of-the-art tool to generate the information on materials properties is to carry out calculations within the density functional theory (DFT). The procedure most often includes optimization of the crystal structure via minimization of the total energy and forces acting on the atoms in a studied system using static calculations at temperature $T=0\text{K}$ followed by the extraction of thermodynamic, elastic, magnetic and other materials properties for the optimized structures. However, this approach, which at present is realized in the form of automatic work-flows for high-throughput calculations, may be problematic if one deals with the so-called dynamically unstable systems. In the dynamically unstable systems frequencies of the lattice vibrations at certain wave vectors are imaginary. Therefore, any distortion of the lattice corresponding to such a wave vector destroys the crystal lattice, and the physical meaning of materials parameters calculated for dynamically unstable crystals artificially stabilized at $T=0\text{K}$ by periodic boundary conditions is unclear [4-5]. On the other hand, anharmonic effects of lattice vibrations sometimes remove the dynamical instability at finite temperature [6] and it has been shown that using DFT-based molecular dynamics simulations rather than static calculations greatly increases the reliability of theoretical predictions of lattice stabilities [7]. However, theoretical predictions of mixing enthalpies from zero-temperatures calculations appeared to be in reasonable agreement with those obtained from the MD simulations [8], and the traditional approach of their simulations with zero-temperature static calculations involving full structural optimization has not been questioned so far.

In this work we present evidences for failure of the static calculations of mixing enthalpies in alloys with the dynamical instability. As a model system, we consider body-centered cubic (bcc) titanium-vanadium alloys that are dynamically and thermodynamically stable at high temperatures in the whole concentration interval, while at low temperatures they cannot exist because of the dynamical/mechanical instabilities [9-10]. Ti-V alloys with the bcc crystal structure are of practical interest for high-temperature structural components for the aerospace and automotive industries as well as for the development of nuclear reactors. Ti and its alloys maintain strength at high temperatures and therefore can be used as construction materials that are subject to high-temperature heating. The alloys are successfully used in surgery tools. Moreover, Ti is also one of the main components of the alloys for cutting tools hard coatings. In principle pure bcc titanium could be a good candidate for high-temperature applications, but it exists only at high temperatures above 1155 K, while it is dynamically unstable at low temperatures. Alloying with vanadium makes it possible to stabilize the high-temperature bcc phase of titanium at temperatures below 1155 K. Therefore, studies of bcc Ti-V alloys and especially analyses of their thermodynamic properties are of great interest.

The reported experimental Ti-V phase diagrams can be divided into two groups: with and without the isostructural phase separation line for the bcc solid solutions, respectively. Murray *et al.* [11] and Nakano *et al.* [12] showed the miscibility gap in the bcc (β -Ti, V) phase and a monotectoid reaction at 948 K: (β -Ti,V) $\leftrightarrow$ (α -Ti) + (V). However, Wei and Fowler [13] suggested that the reported miscibility gap was possibly due to oxygen impurity and argued that neither a miscibility gap nor a stable monotectoid reaction was likely to exist in this system. Nowadays, the Ti-V phase diagram without monotectic reaction is the widely accepted diagram [14-18]. One of the most recent thermodynamic Calphad type assessments of the system was made Ghosh *et al.* [18]. However, the lack and low reliability of the existing experimental thermodynamic data was mentioned in the work and became a reason for higher weight to be given to the experimental data on phase equilibria during the optimization of the parameters. Gosh *et al.* [18] showed that the calculated phase boundaries are in very good agreement with the experimental phase diagram without the miscibility gap (Fig.1). Thus, the accepted binary Ti-V phase diagram shows only three equilibrium phases – liquid, the α -phase (HCP_A3) and the β -phase (BCC_A2). The liquidus and solidus have a congruent minimum at approximately 0.32 mole fraction of V and $T=1878\text{ K}$, the melting points are 1943 K and 2183 K for β -Ti and V, respectively [19-20]. Above the allotropic transformation temperature of Ti (1155K), Ti and V are completely miscible in the (β -Ti, V) solid solution. The solubility of V in (α -Ti) defining the $\alpha/(\beta + \alpha)$ phase boundary was reported by several investigators [21-23]. According Molokanov and Budberg [23], who measured the vanadium solubility in α -Ti using ultra-pure titanium samples, the maximum solubility of V in (α -Ti) is about 0.037 mole fraction around 773-873 K. At room temperature

the equilibrium phases are $\alpha+\beta$. The metastable phases, martensite (α' or α'' , depending on the V concentration) and ω are also encountered in this system [24].

Figure 1. Calculated Ti-V phase diagram [18].

The dynamical instability of Ti and properties of Ti-V system were also studied from first principles. Kadkhodaei *et al.* [25] proposed the Piecewise Polynomial Potential Partitioning (P^4) method to calculate the free energy of mechanically unstable bcc Ti, for which DFT calculations are difficult. They proposed to explore the system's potential-energy surface by discrete sampling of local minima by means of a lattice gas Monte Carlo approach and by continuous sampling by means of a lattice dynamics approach in the vicinity of each local minimum. It was shown that there is reasonable agreement between the free energy obtained for the prototypal example of the bcc Ti and the existing experimental data.

Huang *et al.* [26] computed the formation and stabilization energies of transition metal elements, including α -, β - and ω -phases of Ti. The focus of their work was to understand the influence of transition metal elements on phase diagrams. The authors noted that dynamical instability of bcc Ti at low temperatures made the calculation of the formation energy for the β -phase into a challenging task. Thus, in Ref. [26] the β -phase calculations were carried out under constrain that only the neighbors of the solute were allowed to relax to ensure that the lattice positions in the system as a whole remain close to the bcc crystal structure. The formation energy was found to be negative, which indicated that the solution reaction should be exothermic.

Chinnappan *et al.* [27] calculated the subsolidus equilibrium phase diagram for Ti-V using the cluster expansion technique, lattice dynamics and Monte Carlo methods combined with DFT and found that the formation energies of all the ordered structures are positive, in agreement with the experimental phase diagrams which does not exhibit any ordered intermetallic compound. The formation energies for the hexagonal-close packed (hcp) phases were found to be more positive than for the bcc phases. Computing the phonon dispersion relations and the free energies, the phase boundaries in Ti-V system were found to be in good agreement with reported experimental boundaries.

Elastic constants C' were calculated from first principles as a function of Ti-V composition and the mechanical instability of the bcc alloy in Ti-rich region was observed [10, 28]. It was shown that for Ti metal, the instability is relatively strong and C' is quite negative. However, alloying with vanadium rapidly increases C' and reduces the strength of the instability, in accordance with the behavior of the bcc phase line in the Ti-V alloy. Tegner *et al.* [29] studied the effect of alloying elements on the phase stability and elastic moduli of Ti-alloys and showed that the stabilization of the β -phase was directly correlated with the filling of the d-band.

Uesugi *et al.* [30] calculated the effects of solute X (Mo, Nb, V and W) content on the phase stability of beta-Ti alloys from first principles. The authors showed that while the enthalpies of the α -phases increased with increasing concentrations of Mo, Nb, V and W, the enthalpies of the β -phases decreased with increasing concentrations. This is consistent with the experimental results, showing that Mo, Nb, V and W are beta-stabilizers. The metastable equilibrium concentration was determined, the value for vanadium was ~ 15.6 at%. The mixing enthalpies ΔH obtained using the fully relaxed supercells and data converted from the solution enthalpies were -4 meV and 5.5 meV for 3.7 at.% V and 96.3 at.% V, respectively. Thus, a remarkable change of sign of the mixing enthalpy as a function of V concentration could be expected from calculations presented in Ref. [30]. Is it physical, or could it be an artefact of simulations of dynamically unstable Ti-rich bcc alloys using static calculations at T=0K? Below we resolve this question, theoretically, as well as experimentally, and argue that it should be generally important to take into account the thermal vibrations of the atoms in theoretical predictions of thermodynamic properties, especially for systems with dynamical instability.

2. Theoretical calculations

In this work, we carried out first-principle modeling of disordered Ti-V alloys in the framework of the density functional theory [31]. The exchange-correlation effects were taken into account within the generalized gradient approximation (GGA) [32]. Two methods for the electronic structure calculations were employed, the Exact Muffin-Tin Orbitals (EMTO) method combined with the coherent potential approximation (CPA) [33] and a Projector-Augmented Wave (PAW) method [34] implemented in the Vienna *Ab Initio* Simulation Package (VASP) [35-36]. The EMTO-CPA method allows us to efficiently study the properties of disordered alloys on the fixed underlying crystal lattice. It is not a full-potential method, but it consistently treats the effect of chemical disorder by calculating the alloy Green's function. In the EMTO-CPA calculations the integration over the irreducible part of the bcc Brillouin zone was performed on a 29x29x29 Monkhorst-Pack grid of k-points [37]. The energy integration was carried out in the complex plane using a semielliptic contour comprising 24 energy points. The convergence of energy with respect to the calculation parameters was 10^{-8} Ry.

PAW-VASP calculations were used to take into account the distortions of the underlying crystal lattice in the alloys and for *ab initio* molecular dynamics (AIMD) simulations. The effect of chemical disorder in this case was simulated using 128 atom special quasirandom structures (SQS) constructed as described in [38] on a 4x4x4 bcc supercell with the cubic shape. As the ground state structure of Ti is hcp, the hcp-Ti was also calculated in the 4x4x4 hcp supercell to keep the same number of atoms and to cancel out the numerical inaccuracies. The integration over the irreducible part of the hcp Brillouin zone was found to be converged for the 2x2x2 Monkhorst-Pack k-point grid.

The AIMD simulations were employed to calculate the mixing enthalpy at high temperature T=1300 K. In this case the potential energies were obtained as averages over the AIMD run. For this purpose, we used 9000 time-steps after equilibration (4000 time-steps) with the time-step 1 fs. The AIMD calculations were accelerated by using a two-step procedure. First, the Γ -point calculation was done and then the upsampling procedure [39] to the 2x2x2 grid was performed to get the most accurate results.

In the SQS calculations, formation enthalpy ΔH was determined as

$$\Delta H = E_{Ti(128-n)V} - (((128-n)/128) \cdot E_{Ti} + (n/128) \cdot E_V) \quad , \quad (1)$$

where E_{Ti} and E_V are the energies of the pure Ti and V, respectively, n is the number of vanadium atoms in the supercell, $E_{Ti(128-n)V}$ is the energy of the alloy with n vanadium atoms in the SQS. All the energies were calculated at their respective equilibrium volumes.

Figure 2. Dependence of lattice parameter of bcc Ti-V alloys on V concentration.

The black empty circles denote the values obtained in this work by the EMT0-CPA method. The green filled triangular symbols show the values obtained in this work by the PAW-VASP method at $T = 0$ K. The blue squares are the values obtained by us by AIMD simulations at $T = 1300$ K. The data obtained in [28] by the FP-LMTO method at $T=0$ K are marked with gold triangular symbols. The red stars and the brown triangular symbols correspond to the experimental data from Ref. [40] quenched from 1253 K. The experimental data from Ref. [41] are denoted by pink empty rhombuses. The blue crosses display the experimental results of Ref. [42]. The values of Ref. [43] are indicated by the green empty symbols.

Using the EMT0-CPA and PAW-SQS methods, the thermodynamic properties of the bcc Ti-V alloys were calculated in the whole concentration range. The calculated dependence of the lattice parameter on V concentration in Ti-V alloy is displayed in Fig. 2. At zero temperature EMT0 and PAW calculations for pure Ti and V agree very well with each other. In addition, PAW-SQS and EMT0-CPA calculations for alloys are in agreement with full-potential (FP) LMTO calculations by P. Söderlind et al. [28]. AIMD calculations at $T=1300$ K, as expected, predict higher value of the lattice parameter due to the effect of thermal expansion. Calculated values are in very good agreement with available experiment [40-43]. As one can see, high-temperature calculations show nearly perfect linear dependence of the lattice parameter on the V concentration, indicating that the Vegard's law is fulfilled very well in this system. However, the PAW-SQS lattice parameters calculated at $T=0$ K show small negative deviations from Vegard's law for Ti-rich alloys. They are the first consequence of the failure of the traditional static approach to reproduce thermodynamic properties of dynamically unstable systems. This issue will be discussed in Sec.4 in more details. At this point, it is important to notice that the obtained good agreement between our results and previous calculations, as well as with the experimental studies indicates the reliability of our calculations.

Figure 3 shows the calculated mixing enthalpies for bcc Ti-V alloys in the concentration range from 0 to 100 at. % employing theoretical methods with different level of approximations described above. Starting with the most accepted approach represented in our case by static PAW-SQS calculations including the full optimization of the internal positions of atoms in the supercell, we obtain highly peculiar shape of the mixing enthalpy curve as a function of concentration. While the formation enthalpy is positive for V-rich

alloys and at equiatomic compositions, its values decrease with further decrease of V concentration and becomes negative for alloys with vanadium concentrations below 35 at. %. The enthalpy continues to drop down until ~5% V, followed by an unphysical kink and a rapid increase in Ti-rich alloys. In fact, our results obtained with static PAW-SQS calculations including the full optimization of the internal positions of ions in the SQS are in agreement with predictions made by Uesugi *et al.* [30], discussed in the introduction.

Figure 3. Dependence of mixing enthalpy ΔH on V concentration in bcc Ti-V alloys, calculated in this work with different techniques. The experimental values obtained in the present work at $T=1073$ K (800°C) are shown with purple crosses.

It is worth to point out that the peculiar behavior of the mixing enthalpy appears at compositions which correspond to the region of dynamical/mechanical instability of the bcc Ti-V alloys at zero temperature. Indeed, the bcc Ti-V alloys become mechanically unstable at V concentrations below ~20 at.%, where the elastic constant C' becomes negative [10]. One therefore may suspect that it is related to the instability of the alloys, and therefore is unphysical. On the contrary, our AIMD calculations carried out at high temperature of 1300 K, demonstrate that the alloys become dynamically stable. To verify the dynamical stability of the alloys, we present in Fig. 4 an example of the running average of xx , yy , and zz components of the stress tensor for bcc Ti-V alloy with 6.25 at.% V obtained in an AIMD run at $T=1300$ K. Note that the stress tensor components are equal in all three directions in the simulated system, confirming formally its dynamical stability [7, 44]. In addition, experimentally it is known that the alloys are stable not only dynamically, but also thermodynamically at $T=1300$ K. Considering the mixing enthalpy ΔH obtained in our molecular dynamics simulations at this temperature, one sees positive values in the whole composition

interval (see Fig. 3). Thus, the AIMD results not only quantitatively, but also qualitatively differ from those calculated at T=0K.

Figure 4. Calculated running average of the stress tensor components as a function of the numbers of MD steps for bcc Ti-V alloy with 6.25 at.% V at T=1300 K. σ_{xx} , σ_{yy} and σ_{zz} components of the stress tensor are denoted with red, blue and green lines, respectively.

3. Experiment

As we were unable to find any experimental data on the mixing enthalpy of bcc Ti-V alloys in the literature, we carried out its experimental measurements to answer a question which of the two sets of simulations predict the correct behavior of the mixing enthalpy. Four Ti-V alloys (10, 12, 15, 20 at%V) were produced for the experimental investigation. The purity of the starting materials was Ti-99.98% and V-99.9%. The alloys were melted in an arc-furnace with an unconsumable tungsten electrode on a water-cooled copper hearth in a high purity Ar atmosphere (99.998%). To achieve homogeneity, the buttons were turned over and remelted five times. The weight losses did not exceed 0.2%. For each of these samples, an area scan was performed using microprobe examination in order to control the composition of the resulting alloys. The samples of the alloys were annealed for 24h at 650°C and then for 24h at 250°C in the tube furnace in high purity argon atmosphere. Composition and structure of the samples after the annealing were investigated using SEM and EPMA analysis (Fig. 5) using a TESCAN VEGA LMH microscope with a LaB₆ cathode and an energy dispersive X-ray microanalysis system – Oxford Instruments Advanced AZtecEnergy. For analysis, both backscattered electron and secondary electron imaging were used. A four-crystal wave spectrometer was used during the electron probe microanalysis (EPMA) of all the phases (the analysed particle size was larger than 2 μm). 20 kV was set for the EPMA acceleration voltage. All investigated samples were homogeneous and single phase. The measurement error in determining the concentration of elements using X-ray analysis was 0.05 wt.%.

Figure 5. Microstructure of the alloy Ti-10at%V.

Instrument

In order to obtain experimentally the enthalpies of mixing in the bcc Ti-V alloys, calorimetric investigations were carried out using a drop solution method. Measurements were performed using an isoperibol high temperature Tian-Calvet calorimeter Alexsys 1000 (Setaram, France). The instrument is equipped with 3D sensor which provides high sensitivity and precision. The detailed information about the instrument was published by Navrotsky [45]. Measurements were carried in the high purity protective argon atmosphere (99.998%) in (Al_2O_3) crucibles. The temperature of the calorimetric cell was 800°C . Recording and data processing of the signals from the calorimeter was done using Calisto software [46]. The more detailed information about the methodology of the experiment is described in the work [47].

Calibration

Before and after each series of experiments, the calorimeter was calibrated by dropping small pieces, 5-10 mg, of $\alpha\text{-Al}_2\text{O}_3$ (NIST 720 standard reference material) into an empty crucible. Heat increments between room temperature and the temperature inside the calorimeter (800°C) were calculated from the Standard Reference Material equation [48]:

$$H^\circ_T - H^\circ_{273.15} = AT^{-2} + BT^{-1} + C\ln T + K + DT + ET^2 + FT^3 + GT^4 + HT^5 \text{ (J/mol)}, \quad (2)$$

where $A = +6.6253\text{E}+07$, $B = -4.54238\text{E}+06$, $C = -5.475599\text{E}+04$, $D = +2.574076\text{E}+02$, $E = -8.57516\text{E}-02$, $F = +4.299063\text{E}-05$, $G = -1.15192\text{E}-08$, $H = +1.26351\text{E}-12$, $K = +2.5819702\text{E}+05$.

A series of 5 successful drops was used to calculate the calibration factor, measured to be $0.00455 \pm 0.78\%$ J/ $\mu\text{V/s}$.

Measurements

A bath of pure Ga of 99.9999% was used as a solvent. The choice of the bath was based on several considerations:

- The number of moles of solvent was far greater than the number of moles of solute such that the solvent bath would be close to an infinitely dilute solution even after all samples have been dropped.
- A fast and complete solution of the sample (or standard) is required.
- Pure gallium has sufficient solubility for titanium and vanadium. Furthermore, it is possible to add several at.% of Ti and V without precipitation of a solid intermediate compound.

The mass of the solvent was 15-20 g. During the experiment, drops were done successively into the solvent bath. The composition of the bath at the end of the experiments was close to pure gallium. In the area of dilute solution, the partial enthalpies of formation of the pure elements and the investigated

compounds in liquid gallium is effectively independent of composition. This made it possible to determine average values for the enthalpy of solution of each material in liquid gallium.

The following thermodynamic cycle was used in order to derive the enthalpies of mixing of bcc Ti and bcc V:

Consequently the mixing enthalpy between BCC_A2 Ti and BCC_A2 V can be obtained as :

$$\Delta H_1 = -\Delta H_8 - \Delta H_7 - \Delta H_6 + \Delta H_5 - \Delta H_2 + \Delta H_3 + \Delta H_4$$

where

- $\Delta H_1, \Delta H_2, \Delta H_3, \Delta H_4, \Delta H_5, \Delta H_6, \Delta H_7, \Delta H_8$ are the heat effects connected with the reactions, given by Eqs. (3)-(10) correspondingly.
- $\Delta H_2, \Delta H_3, \Delta H_4$ – Measured thermal effects
- $\Delta H_5, \Delta H_6, \Delta H_7, \Delta H_8$ – thermal effects calculated using pure elements database [49].

The results of the heat of dissolution of pure Ti and V in the liquid Ga (in accordance with the reactions (5) and (6)) are presented in Table 1 and the heat of formation of bcc Ti_xV_y alloys (in accordance with reaction (4)) are presented in the table 2.

Table 1 Heat effects Q^a after drops of pure elements Ti and V with mass m , from temperature T_r to temperature of solvent^b $T_s = 800^{\circ}C$ at 0.1 MPa under an Ar-atmosphere

Sample	m,mg	$T_r / ^{\circ}C$	Concentration in bath after drop (at.%)	Q, J/mol
Ti	6.27	24.5	0.02	21908
	8.05	24.5	0.05	21603
	8.04	24.5	0.08	21536
	7.97	24.5	0.10	21397
V	9.21	29.5	0.03	20536
	9.77	29.5	0.066	20826
	8.05	29.5	0.09	20230
	14.6	29.5	0.14	20809
	11.9	29.5	0.18	20582
^a Q is the heat effect associated to dissolution of solid at T_r in liquid Ga at T_s . ^b Ga with mass 19 - 20 g was used as a solvent.				

Table 2 – Heat effect Q^a after drops of the investigated alloys with mass m , from temperature T_r to temperature of solvent^b $T_s = 800^{\circ}C$ at 0.1 MPa^c under an Ar-atmosphere

Alloy	m, mg	$T_r, ^{\circ}C$	Concentration in bath after drop (at.%)	Alloy composition ^c , at.%		Q_1 , J/mol
				Ti	V	
Ti-10V	18.5	32	0.06	90.2	9.8	22022
	13.27	32	0.11			21882

	15.86	32	0.16			21940
	5.26	32	0.18			22057
	13.56	32	0.23			21919
Ti-12V	6.54	32.3	0.02	88.1	11.9	22078
	11.45	32.3	0.06			22102
	7.58	32.3	0.09			22017
	12.43	32.3	0.13			22115
	13.31	32.3	0.177			21994
Ti-15V	8.75	31.9	0.03	85.2	14.8	22323
	9.21	31.9	0.06			22308
	8.13	31.9	0.09			22015
	11.05	31.9	0.13			22382
	7.99	31.9	0.156			22136
	9.56	31.9	0.19			21988
	20.23	31.9	0.26			22605
Ti-20V	4.28	28.8	0.015	79.9	20.1	22437
	6.8	28.8	0.04			22482
	8.9	28.8	0.07			22386
	8.25	28.8	0.10			22300
^a Q is the heat effect associated to dissolution of solid at T _r in liquid Ga at T _s						
^b Ga with mass19 - 20 g was used as a solvent.						
^c Standard uncertainty of the alloy composition measurements was less than 0.1 at.%.						

The resulting values for the enthalpy of mixing of the bcc Ti and bcc V at 800°C (Table 3) are positive in the investigated concentration range. An increase of the vanadium concentration in the alloys leads to even more positive values in the enthalpies of mixing, and this additionally confirms the existence of the large miscibility gap in the solid BCC_A2 phase which was reported as a conclusion of the system review made by Murray [14]. The results from Fumin and Flower [13] suggesting the absence of a miscibility gap and a continuously decreasing $\alpha+\beta/\beta$ transus with increasing vanadium concentration does not seem to be realistic.

Table 3 Mixing enthalpies in the bcc phase in Ti-V system at 800°C relative to both elements in the bcc phase

Alloy	ΔH_{mix}	
	J/mol	eV
Ti-10V	1100 ± 141	0.0114
Ti-12V	1200 ± 132	0.0124
Ti-13V	1300 ± 191	0.0135
Ti-20V	1590 ± 147	0.0165

4. Discussion

Let us now return to Fig. 3 which summarizes mixing enthalpy ΔH as a function of V concentration in bcc Ti-V alloys calculated in this work with different techniques and compare the results of the simulations with our experimental measurements. One clearly sees that the experimental data is in good agreement with results obtained by AIMD simulations. At the same time, the experiment clearly indicates that static calculations at T=0K with full structural optimization predict qualitatively wrong behavior of the mixing enthalpy in bcc Ti-rich Ti-V alloys.

To understand the failure of the zero-temperature calculations of ΔH in dynamically unstable systems, let us consider the simplest case of a single V impurity in bcc Ti, and compare the atomic positions obtained upon static relaxations of the corresponding supercell at zero temperature with mean atomic positions calculated from AIMD simulations carried out at 1300 K. The results of the simulations are shown in Fig. 6 (a) and (b), respectively.

Figure 6. Two-dimensional projection onto the x-y plane of bcc Ti-V alloys modelled as a 128 atom supercell with a single V impurity (red square) and 127 Ti (green crosses) atoms (a) obtained by static relaxation of the supercell at 0 K and (b) from AIMD at 1300 K as the time-average of the atomic positions.

One can see that at 0 K the almost all the Ti atoms in the supercell move out of the ideal bcc positions upon the static relaxation. The effect is much more pronounced than upon static relaxations of host atoms around impurities in dynamically stable systems, which are usually significant for nearest neighbors of the impurity [50]. In fact, it appears that the relaxations create an artificial non-bcc structure within the considered $4 \times 4 \times 4$ supercell. In fact, this effect must be expected in a dynamically unstable system. Indeed, in pure bcc Ti forces on atoms placed at ideal sites of the bcc crystal lattice should vanish due to the lattice symmetry. However, any perturbation of the symmetry, like the presence of V impurity in our case, must destroy the dynamically unstable system. Moreover, if the shape of the supercell would not be conserved during the simulation, the structure would transform into the more stable one, most likely into ω -phase. However, due to the limited size of the supercell and our focus on the mixing enthalpy of bcc Ti-V alloys, we do not investigate this issue further in the present work. The relaxations decrease the total energy of the supercell (compare the mixing enthalpy curves obtained for relaxed and unrelaxed PAW-SQS calculations) and contribute greatly to the stabilization of the simulated phase. However, it is unlikely that the relaxed supercell serves as a reasonable model of the bcc phase.

On the contrary, the average atomic positions obtained in AIMD simulations at 1300 K are close to the ideal bcc lattice positions, as can be seen in Fig. 6 (b). This is an additional justification of the dynamical stability of the alloy [7, 44] and is also in agreement with experimentally observed thermodynamic stabilization of bcc Ti-V alloys at high temperature. Consequently, contribution to the potential energy of the system from local lattice relaxation decreases. One sees in Fig. 3 that the AIMD results for the mixing enthalpy at high temperature are in reasonable agreement with zero temperature calculations, which neglect the effects of local lattice relaxations: ΔH calculated by the PAW-SQS method with atoms occupying ideal bcc lattice positions and by EMT-CPA at 0 K agree with each other and show positive values and a qualitatively correct upward curvature over the whole concentration range. Of course, they still lie above the AIMD and experimental points, i.e. the curvature of ΔH calculated at $T=0$ K for Ti-rich alloys without local lattice relaxations is apparently overestimated.

Interestingly, for dynamically stable V-rich bcc Ti-V alloys the results of AIMD simulations at high temperature are closer to ΔH calculated at $T=0$ K without local lattice relaxations than to fully relaxed

calculations. To verify that this is a physical effect rather than an indication of an inconsistency in our finite-temperature calculations, we carried out AIMD run for the dynamically stable bcc $\text{Ti}_{25}\text{V}_{75}$ alloy at $T=300\text{K}$, and calculated its mixing enthalpy with respect to bcc V and hcp Ti (the bcc phase of Ti cannot be simulated at such a low temperature because of its instability). A comparison with static calculations presented in Fig. 6 shows excellent agreement between AIMD and static calculations at this composition, indicating internal consistency of our simulations at zero and at finite temperatures. Higher positive values of ΔH calculated at $T=1300\text{ K}$ for bcc $\text{Ti}_{25}\text{V}_{75}$ alloy in comparison to $T=0\text{ K}$ static calculations shown in Fig. 2 can be explained by the fact that the magnitude of local lattice relaxations (understood as deviations of the mean positions of atoms at finite temperature from the sites of the underlying bcc crystal lattice) decreases with temperature, as has been demonstrated by Hellman [51]. Therefore, their contributions to the potential energy of the alloy decreases as well, making ΔH obtained with AIMD larger and in better agreement with static calculations that neglect the effect of local lattice relaxations.

Fig. 6. Dependence of the mixing enthalpy on V concentration in bcc Ti-V alloys with respect to bcc V and hcp Ti. ΔH value for bcc $\text{Ti}_{25}\text{V}_{75}$ alloy obtained by AIMD simulations at $T = 300\text{ K}$ is shown as purple filled triangular symbols. ΔH values obtained by PAW-SQS method with the full optimization of ion positions in the SQS at $T = 0\text{ K}$ are indicated by green solid line with triangles.

5. Conclusions

We have addressed a problem of predictions of thermodynamic properties of alloys with dynamical instability from first principles. We have considered bcc Ti-V alloys which are dynamically unstable at low temperature and V concentration. This, together with their high technological importance, makes them into the perfect model system for the study. The mixing enthalpies of the studied system, the key materials parameter for a description of phase stability and phase transformations in alloys, have been calculated at zero and high temperatures as a function of the vanadium concentration and measured at 1073 K using an

isoperibol high temperature Tian-Calvet calorimeter. We found that the enthalpies of mixing calculated at high temperature using AIMD are positive for all V concentrations, in contrast to the traditional static calculations with full relaxation of atomic positions at $T=0\text{K}$, which predict negative values for alloys with low vanadium concentrations. Moreover, calculations of the mixing enthalpy at high temperature give much better agreement with the experimental data measured in this work. The failure of the accepted zero temperature static approach is linked to the dynamical instability of the bcc phase of Ti and its alloys at 0 K. Considering single V impurity in bcc Ti, we have demonstrated that the supercell with the relaxed structure cannot be used as a model of the bcc phase. Our work shows that it is important to take into account lattice vibrations in theoretical predictions of thermodynamic properties, especially for systems with dynamical instability.

Acknowledgements

The support from the Swedish Research Council grants No 2015-04391 and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No 2009 00971) is gratefully acknowledged. We used computational resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC). Theoretical calculations of the mixing enthalpy were supported by the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST “MISIS” (No K2-2019-001) implemented by a governmental decree dated 16 March 2013, No 211. The calculations were performed at the supercomputer cluster provided by the Materials Modeling and Development Laboratory at NUST “MISIS”. Experimental measurements of the mixing enthalpy were supported by the Russian Science Foundation (Project No. 18-12-00492).

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