Electrons Meet Alloy Development: A γ-TiAl-Based Alloy Showcase

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Density functional theory is a workhorse of present electronic structure calculations. These are increasingly more applied in materials science as they allow for insight beyond experimental capabilities, testing hypotheses, or isolating various phenomena. Herein, an overview of the applications of the electronic structure calculations applied to extracting alloying trends, which, in turn, leads to refining of alloys, is presented. The topic covers the construction of structural models by properly considering site preference. Next are discussed alloying trends in structural and mechanical properties. The final part deals with microstructure features such as extended defects or multiphase constitutions. The unifying themes of the presented application are compositional trends in properties of lightweight intermetallic γ-TiAl-based alloys.

1. Introduction

Many recent high-tech applications have been enabled by discovery, exploration, and mastering synthesis of novel material systems. For example, gallium nitride is the key to BluRay technology and efficient solid lighting,[1] which was awarded the Nobel Prize in Physics in 2014.[2] The 2010 Nobel Prize in Physics was awarded for isolating graphene, a prototype 2D material, eventually leading to 2D (flexible) electronics.[1] More recently, the 2019 Nobel Prize in Chemistry was awarded for the development of lithium-ion batteries.

Those few examples fall under the overarching roof of materials science. They demonstrate its interdisciplinary nature, an almost infinite variety of materials, and its appearance in everyday life.

An integral part of modern materials discovery is modeling. The available methods are diverse, and none of them are superior to the others. Similarly to experiments, theoretical modeling requires choosing an appropriate method to tackle the problem of choice. The critical parameter is the length and time scale of the studied phenomenon (Figure 1). Starting from the macroscopic scale, typical problems related to mechanical response or heat conduction in final products are described using continuum mechanics, partly using phenomenological models. Mesoscale problems involve microstructure evolution and its development upon material synthesis/application. Prominent examples are phase diagram predictions and phase-field modeling, homogenization techniques for including material texture, or prediction of defect structure evolution (e.g., discrete dislocation dynamics). For an overview of microstructure modeling techniques demonstrated as examples of Ti alloys, the reader is referred to a recent review by Zhang et al.[4] On the next smaller length scale, individual defects are conveniently treated using molecular statics/dynamics simulations which yield predictions about their impact on phase stability, mechanical properties, diffusion, precipitation, and segregation, to name a few. Answering questions of “why an element has a specific effect” usually requires a deeper analysis of the chemical bonding using electronic structure methods. To highlight the state of the art of nanoscale modeling, let us recall the 1998 Nobel Prize in Chemistry “for development of the density-functional theory/computational methods in quantum chemistry,” as well as the 2013 Nobel Prize in Chemistry “for the development of multiscale models for complex chemical systems” (molecular dynamics).[5]

Much electronic structure research deals with nanoscale applications in novel electronics. In contrast to that, in this article, we will review recent activities on modeling material problems related to structural alloys developments, that is, topics related to classical metallurgy. Here, electronic structure modeling augments experimental techniques by providing insight into the most fundamental quantum mechanical level. It also allows for high-throughput screening and machine-learned approaches, which eventually lead to change from experience-based to knowledge-based (or data-driven) material exploration. To narrow and make uniform the discussed examples, we exclusively focus on topics related to TiAl intermetallic alloys.

1.1. Alloys: Elements, Phases, Microstructure, Processing

An alloy is a mixture of several elements, typically metals. Regions with homogeneous chemistry and material properties are called phases. Those are often crystalline; the same
composition can be realized by different allotropes, that is, crystals with a different crystal structure. An example of temperature-induced allotrope transformation is titanium: the low-temperature hexagonal close-packed structure \( \alpha \)-Ti transforms to high-temperature body-centered cubic \( \beta \)-Ti at about 882 °C.\(^5\) Spatial regions of one phase with a continuous lattice are called grains. Such homogeneous zones (grains) are usually separated by regions with typically lower crystalline order, called grain boundaries. Shape, orientation, and distribution of grains (of one or more phases) comprise a microstructure or material. Obviously, it is not only the physical properties of the individual (crystalline) grains but, equally important, the microstructure itself that dictates the overall material behavior at the macroscopic scale. The microstructure can be controlled via the synthesis process itself or post-synthesis heat treatment, which could lead, for example, to precipitation hardening of phases,\(^6\) grain growth,\(^7\) or segregation-triggered grain boundary strengthening.\(^8\)

Much insight can be obtained from the experiment alone, which has the unbeatable advantage of characterizing the “real” material. However, experimental investigations are costly and time-consuming (particularly when it comes to characterizations at nanoscale). Moreover, there are physical properties which still remain inaccessible for experimental measurements (e.g., information about metastable phases, full compositional control, etc.). Here, electronic structure methods based on quantum mechanics provide unbiased information at the (sub-)atomic scale. A treatment of the whole microstructural development using atomistic and electronic structure methods is impossible due to model size and simulation time restrictions. Nevertheless, modeling can provide useful hints on, for example, change of the bonding character and elastic properties by alloying,\(^9\) preferred phase for alloying element partitioning,\(^10,11\) or segregation to grain boundaries.\(^12\) Such information, in turn, helps to guide the experimental efforts and/or narrows the set of possible candidates for alloying. Consequently, the true power of the electronic structure methods is combined with experimental investigations and/or other modeling techniques.

1.2. \( \gamma \)-TiAl-Based Alloys

TiAl intermetallic alloys based on the \( \gamma \)-TiAl phase are lightweight structural materials with many extraordinary properties. They exhibit good oxidation resistance, high strength, and creep resistance.\(^13,14\) These alloys excel at high temperatures, and hence the primary application domains are automotive and aerospace industries.\(^14,15\) The main constituting phases are (slightly) tetragonal \( \gamma \)-TiAl (L1\(_0\), space group no. 123, \( P4/\text{mmm} \)) and hexagonal \( \alpha\)-Ti\(_3\)Al (D0\(_{19}\), space group no. 194, \( P6_3/\text{mmc} \)), see Figure 2. However, alloys containing only those phases suffer from insufficient hot workability, and therefore ternary alloying elements are added to open a possibility for more phases in the microstructure and thereby for better hot workability. Namely, the presence of bcc phase (\( A_2 \), space group no. 229, \( \text{Im}\overline{3}m \)) was proposed to overcome the limitations of the binary system. Among known \( \beta \) stabilizers are Nb and Mo, which are the major alloying elements in so-called T stands for TiAl, N for Nb and M for Mo (TNM) alloys.\(^16\) Further optimizations included small additions of C and Si for enhanced creep properties. Those alloys are known as TNM and TNM\(^\ast \)

**Figure 1.** Different modeling techniques are suitable for different length scales and hence to address different problems. Left-to-right: finite-element method (FEM) using continuum mechanics showing strain distribution in a blade made of TiAl–Nb alloy,\(^134\) example of mesoscale modeling of dendrite growth in a \( \beta \)-solidifying TiAl alloy using phase-field modeling,\(^135\) nanoscale atomic simulation of a room-temperature tensile test of \( \gamma \)-TiAl, and valence charge distribution of (0001) plane of \( \alpha \)-Ti\(_3\)Al. Reproduced under the terms of the CC BY 4.0 license.\(^134\) Copyright 2020, Xiaopeng Wang, Wenchen Xu, Peng Xu, Haitao Zhou, Fantao Kong, and Yuyong Chen. Reproduced with permission.\(^135\) Copyright 2020, Elsevier.

**Figure 2.** Visualization of the TiAl structures discussed in the present work.
alloys was significantly shortened with the aid of knowledge-based alloy design. A vital role played thermodynamic CALPHAD modeling, which allows for fine tuning of the final compositions.\[16\] Semiempirical continuum models further supported the thermodynamic methods.\[17\] However, these modeling techniques require inputs regarding structural, mechanical, and thermodynamic properties of individual constituting phases as functions of their composition. The electronic structure methods are well suited for this task, as will be demonstrated in this article.

1.3. Electronic Structure Modeling

Electronic structure methods, also known as first-principles or ab initio methods, fundamentally rely on quantum mechanics. However, the wave-function formalism implied by direct application of the Schrödinger equation to a many-body system of interacting electrons and nuclei turns out to be mathematically infeasible. In 1927, Fermi and Thomas proposed a treatment in which the role of a central quantity takes charge density instead of the wave function.\[18,19\] The modern density functional theory (DFT) was then formulated in the mid-1960s\[20,21\] and since then has become the workhorse of nearly all ab initio calculations in materials science and physics.

Quantum mechanical exchange and correlation electron–electron interactions have to be approximated. The two most common approaches are local density approximation (LDA) and generalized gradient approximation (GGA), wherein for the latter electron interactions have to be approximated. The two most popular DFT codes. VASP and a majority of other DFT software packages utilize for the description of the ion–electron interactions.\[22\] The VASP software package was chosen primarily for its robustness and ease of use; it has become one of the most popular DFT codes. VASP and a majority of other DFT codes used in materials science science solve the many-electron problem in the reciprocal space, which is enabled by assumed underlying crystalline periodicity.

Each lattice site in the atomic model entering the VASP calculation is occupied exactly by one atom (as in nature). Periodic boundary conditions (PBCs) imply that a simulation box can be restricted to only one unit cell at a time. This is very convenient for single-element and ordered phases, where a unit cell contains only one unit cell at a time. This is very convenient for single-element and ordered phases, where a unit cell contains more lattice sites than the Al sublattice of the \(\alpha\)-TiAl and \(\gamma\)-TiAl phase. The vertical line \(m\)–\(X\) in the \(\gamma\)-TiAl structure also consists of two sublattices, Al and Ti. In contrast to \(\gamma\)-TiAl, where both sublattices contain the same number of lattice sites, the Ti sublattice consists of three times more lattice sites than the Al sublattice of the \(\alpha\)-TiAl phase. The situation becomes even more complicated for other stoichiometries. For example, the cubic \(L1_2\) structure consists of two sublattices, one Al and one Ti. Similarly, the \(\alpha\)-TiAl phase (\(DO_{19}\) structure) also consists of two sublattices, Al and Ti.

2. Building Structural Models

2.1. Site Preference

When alloying elements into single-species phases, such as face centred-cubic (fcc) Al or hexagonal close-packed (hcp) Ti, one has to estimate whether the solute atoms occupy interstitial or substitutional positions. The latter is a simple substitution of the solvent atom for the solute element. The situation is more complicated when the phase consists of several sublattices. Each sublattice is a collection of lattice sites that are symmetry equivalent. For example, the \(\gamma\)-TiAl phase (\(L_1_2\) structure) consists of two sublattices, one Al and one Ti. Similarly, the \(\alpha\)-TiAl phase (\(DO_{19}\) structure) also consists of two sublattices, Al and Ti. In contrast to \(\gamma\)-TiAl, where both sublattices contain the same number of lattice sites, the Ti sublattice consists of three times more lattice sites than the Al sublattice of the \(\alpha\)-TiAl phase. The situation becomes even more complicated for other stoichiometries. For example, the cubic \(L1_2\) structure of TiAl contains two symmetry nonequivalent Al sites, thus forming two Al sublattices (Wyckoff positions 2b and 4c). Further complications appear by symmetry breaking due to defects, such as interfaces and grain boundaries.\[12\]

It is essential to estimate which sublattice is preferentially occupied by the alloying element X for building representative models. Let us consider an example of a phase with only two sublattices, represented by a supercell \(T_{m}^{\alpha}\) [Al\(_{n}\)]. The vertical line \(m\) is used to separate the two sublattices. We compare the energy of a system with solvent atom X on the Ti sublattice, \(T_{m-n}^{\alpha}X\) [Al\(_{n}\)], with a scenario where X is on the Al sublattice, \(T_{m}^{\alpha}\) [Al\(_{n-1}\)X]. These two scenarios, however, do not have the same number of Al and Ti atoms, and hence the energy comparison will depend on the...
actual chemical potentials of Ti and Al. To circumvent this, we consider additionally antisite defects: Ti antisites (Ti atom on the Al sublattice, Ti\text{m}\text{\_}\text{Al}\text{\_}X) and Al antisites (Al atom on Ti sublattice, Ti\text{m}\text{\_}Ti\text{\_}Al\text{\_}X). Consequently, we obtain two cases: Ti-rich (Al-rich) with more Ti (Al) atoms in the system. The below definitions of the corresponding two site-preference energies are schematically shown in Figure 3.

$$E_{\text{site}}^{\text{Ti-rich}}(X) = E(X \rightarrow Ti) + E(X \rightarrow Ti) - E(Ti \rightarrow Ti)$$  \hspace{1cm} (1)

$$E_{\text{site}}^{\text{Al-rich}}(X) = E(X \rightarrow Al) + E(X \rightarrow Al) - E(Al \rightarrow Al)$$  \hspace{1cm} (2)

If $E_{\text{site}}^{\text{Ti-rich}}(X) < 0$ and $E_{\text{site}}^{\text{Al-rich}}(X) < 0$, X preferably occupies the “deficient sublattice” and we speak about compositionally dependent site preference: X sits on Al (Ti) sublattice for Ti-rich (Al-rich) compositions. If $E_{\text{site}}^{\text{Ti-rich}}(X) < 0$ and $E_{\text{site}}^{\text{Al-rich}}(X) > 0$, element X preferably sits on Ti (Al) sublattice even if this leads to creation of the antisite defect for the Al-rich compositions. In this case, we speak about strong Al sublattice preference. Analogously, strong Ti sublattice preference corresponds to $E_{\text{site}}^{\text{Ti-rich}}(X) > 0$ and $E_{\text{site}}^{\text{Al-rich}}(X) < 0$. Finally, if both site-preference energies in Equation (1) and (2) are positive, the system is unstable in its original configuration, as the system with antisite defects is energetically preferred over the perfect one, as demonstrated by a negative value of so-called exchange energy, $E_{\text{site}}^{\text{exc}}$:46

$$E_{\text{site}}^{\text{exc}} = \frac{E(Al \rightarrow Ti) + E(Ti \rightarrow Al)}{2}$$  \hspace{1cm} (3)

Site preference for bulk TiAl phases has been reported in numerous studies,47–49 which differ by how the site preference is evaluated. Benedek et al.48 and Holec et al.50 used the concept of formation energy change but used different chemical potentials. Gehringer et al.12 instead used the earlier-defined compositional-dependent site-preference energies and transferred them into a single-value quantity as

$$E_{\text{site}}(X) = \frac{1}{2} \left[ E_{\text{site}}^{\text{Ti-rich}}(X) - E_{\text{site}}^{\text{Al-rich}}(X) \right]$$  \hspace{1cm} (4)

Those results are shown in Figure 4. Though the different approaches yield different absolute values of $E_{\text{site}}$ (which is related to the different definitions/meanings of this quantity), the predicted trends are essentially the same. All 3d, 4d, and 5d transition metal (TM) solute atoms preferably occupy the Ti sublattice of the α₂-Ti₃Al phase, the only exception being the group 11 elements (Cu, Ag, Au). Unlike that, the site preference changes strongly in the case of γ-TiAl. While the early TM (groups 3–5) prefer Ti sublattice, the later TMs (groups 7–11) tend to occupy Al sublattice.

The earlier-described 0 K treatment can be extended to finite temperatures using equilibrium thermodynamic considerations.51,52 Not only was Jiang51 able to show that, for example, Nb shows much stronger Ti sublattice preference than Mo in γ-TiAl, a conclusion consistent with other reports (e.g., see the study by Holec et al.50), but it also clearly showed that the site preference gets more pronounced with increasing temperature or can even change with temperature in the case of off-stoichiometric compositions. The reason for this is the inclusion of (temperature-dependent) configurational entropy.53 This approach was recently further improved by including defect interaction energies,52 as applied to the case of Nb in γ-TiAl, again demonstrating the strong Ti sublattice preference of Nb.

It is worth noting that the situation gets further complicated in the case of crystal imperfections such as interfaces, grain boundaries, surfaces, or dislocations. For example, creating an α₂/γ interface53 leads to splitting the Ti sublattice (Al sublattice) in the α₂-TiAl (γ-TiAl) side of the interface into two symmetry non-equivalent subsets of Ti (Al) sites.12 These need to be both considered separately for complete site preference evaluation. Furthermore, this could lead to a change of the site preference at the interface/grain boundary concerning the preferred site in the bulk of the phase, constituting an additional barrier for solute atom segregation. Such analysis is beyond the present discussion, and the reader is referred to a recent publication.12

2.2. Phase Transformations

Inspecting the Ti–Al phase diagram containing numerous phases,54 one is not surprised that various phase transformations occur depending on the actual composition and
temperature. Those are important for actual microstructure development.\textsuperscript{[14]} For more information about phase transformations, the reader is referred to excellent textbooks, either a general one such as the book by Porter et al.\textsuperscript{[55]} or a more specific one devoted to Ti alloys such as the book by Banerjee et al.\textsuperscript{[56]} Apart from more conventional phase transformations such as decomposition and growth, also ordering\textsuperscript{[57]} and diffusionless\textsuperscript{[58–60]} transformations have been reported in the literature for Ti–Al–Mo model alloys. Those latter examples are especially well suited for atomistic modeling, which can provide energy landscapes and thereby transformation paths and barriers.

Molybdenum is used as a β-stabilizer as the pure β\textsubscript{o} phase (B2 structure, CsCl prototype) and its disordered counterpart are not stable and do not appear in the equilibrium phase diagram.\textsuperscript{[61]} The β\textsubscript{o}, TiAl phase is dynamically unstable, which means that any distortion such as atom displacements by thermally induced phonons induces phase transformation.\textsuperscript{[50]} The β\textsubscript{o} phase is connected to the stable γ-TiAl via Bain’s transformation path, exhibiting no energy barrier,\textsuperscript{[56,62,63]} and hence would lead to a spontaneous β\textsubscript{o} → γ diffusionless phase transformation. Upon introducing chemical disorder, the Born–Oppenheimer potential energy surface flattens, hence reducing the driving force for spontaneous transformation. Interestingly, the chemical disorder contributes also towards the dynamical stabilization of the β phase, as the phonon density of states (DOS) corresponding to imaginary frequencies is significantly reduced compared with the ordered β\textsubscript{o} phase.\textsuperscript{[50]}

Adding Mo leads to stabilizing the β phase. Abdoshahi et al.\textsuperscript{[64]} showed that β\textsubscript{o} phase becomes energetically preferable over γ-TiAl for Mo content above ≈ 8 at.% and that Bain’s transformation path is barrierless again. The optimum amount of Mo, for which β\textsubscript{o} is most stable, was predicted to be around ≈ 18 at.%\textsuperscript{[50]} (see Figure 5 for the ordered structures), and is in agreement with the experimentally determined equilibrium Mo concentration of 16.3 ± 2.6 at%.\textsuperscript{[58]} The chemical disorder was shown recently to result in the appearance of small (≤ 10 meV/atom) energy barriers, hence preventing a spontaneous phase transformation between chemically disordered bcc (β) and fcc (γ\textsubscript{dis}) phases.\textsuperscript{[64]}

A trignonal deformation path can also connect the two latter structures.\textsuperscript{[62,63]} However, this results in a significant increase of the transformation barrier (≈ 80 meV/atom) and has therefore been suggested not to be operational.\textsuperscript{[64]} Trignonal path applied to the ordered β\textsubscript{o} phase results in ≥ 500 meV/atom barriers,\textsuperscript{[62–64]} which effectively discriminate this transformation mechanism. Moreover, the final state is not the thermodynamically stable γ-TiAl (L1\textsubscript{o} structure) but a differently ordered L1\textsubscript{1} structure.

Another diffusionless transformation, which has been experimentally observed\textsuperscript{[59,65]} is the β → α transformation. This is a known process for Ti-base alloys\textsuperscript{[66]} and has also been theoretically studied for some binary systems, for example, Ti–Ta.\textsuperscript{[67,68]} Abdoshahi\textsuperscript{[69]} showed that the β → α transformation for Ti\textsubscript{0.5}Al\textsubscript{0.5} proceeds again in a barrierless manner for the ordered phases (β\textsubscript{o} → B19, Figure 5), while chemical disorder is flattening the potential energy surface. Here, apart from the cell shape change (as in Bain’s transformation path), atomic planes in the unit cell are mutually shuffled. It turns out that in the beginning of the β → α transformation, shuffling is a dominant process, whereas near the hexagonal α structure, the cell shape changes dominate. Moreover, Mo stabilizes the β phase, leading to barrierless α → β (or B19 → β\textsubscript{o}, Figure 5) transformations for Mo content ≥ 10 at.%.

Ordering transformation is yet another critical transition occurring when the alloy is cooled. An example of this is the β → β\textsubscript{o} transformation experimentally reported for the Ti–Al–Mo system.\textsuperscript{[57,70]} The 0 K energy differences between ordered and disordered phases allow estimating the impact of Mo on the ordering temperature. While the exact ordering temperature scatter significantly depend on the method used (plane wave VASP-SQS or EMTO–CPA), the composition-dependent trend seems to clearly suggest an increase in $T_{\text{ord}}$ with increasing Mo content.\textsuperscript{[60]} This is in line with the experimental measurements,\textsuperscript{[57]} as well as a more detailed study including multisite interactions and conducting explicit Monte Carlo simulations.\textsuperscript{[71]}

There are also other studies using Monte Carlo simulations and focusing on order/disorder transitions in Ti(Al)-based systems. For example, Gunda and Van der Ven\textsuperscript{[57]} studied impact of substitutional Al and interstitial O on Ti alloys. Using DFT calculations, they parameterized ternary CE and could show that the ordering temperature between disordered α-Ti(Al, O) and ordered α\textsubscript{1}Ti\textsubscript{1}Al\textsubscript{1}O\textsubscript{1} phases strongly depends on the O chemical potential, which determines how much of O is dissolved in the system. With increasing O content, the ordering temperature significantly drops. Another recent example is the work of Körmann et al.\textsuperscript{[73]} They applied DFT to parameterize machine-learned interatomic potentials (MLIPs) in a quaternary TiAlNbV high-entropy alloy (HEA). Subsequently, they used those MLIPs to conduct Monte Carlo (MC) simulation, suggesting that the bcc HEA tends to order below ≈ 1700 K into the β\textsubscript{o} phase with the B2 structure.

2.3. Refining Structures

Ab initio calculations can be used to test hypotheses that are difficult to be resolved experimentally. One such example is shortly described.

The Ti–Al binary system is rich in phases and becomes even richer when additional alloying elements are included. For example,
Nb is usually added for the system to proceed upon cooling through the β phase field, which is desirable for alloy workability.\[^{16}\] However, high Nb content leads also to the precipitation of an orthorhombic O phase.\[^{74}\] Another strong stabilizer is Mo, for which the appearance of a different orthorhombic phase, B19, has been reported as a transition phase upon decomposition of β, to α₁ + γ structures.\[^{79}\] B19 phase has also been reported for Nb.\[^{76}\] The basic difference between B19 (nominally TiAl) and O phase (namely Ti₂AlNb) stems from a different occupation of some sites.\[^{75}\] Energy differences are essentially zero (the two phases, Mo-alloyed in a dissolution\(^\text{Figure 6b}\), we see that when for low Mo content, the energy differences are essentially zero (the two phases, Mo-alloyed B19 and Mo-deficient Ti₂AlMo O phase, are in fact identical), and for larger Mo content, we predict the O phase to be energetically preferred over the B19 phase. This can also be interpreted as a driving force for Mo ordering because it couples with Ti neighbors, leading eventually to formation of Al sublattice in the O phase. It should be mentioned, however, that the energy differences are very small (≈ 16 meV/atom for 15.5 at.% Mo), which could be easily overruled by temperature effects (\(k_B T \approx 26\) meV at \(T = 300\) K).

2.4. Chemistry of Bonding

The great advantage of the electronic structure methods is that they can provide insight into the bonding mechanisms. This is usually done by analyzing the electronic DOS and/or charge density.

Liu et al.\[^{77}\] studied the electronic structure of sheared γ-TiAl and α₁-Ti₃Al phases. The dominant Al-3p–Ti-3d covalent bonds in the γ phase, responsible for its brittleness and higher shear stress compared with the α₁ phase, are weakened upon shearing, whereas this binding is strengthened in the α₁ phase. Thereby, the alloys with the two-phase microstructure exhibit improved mechanical properties in comparison with the single phases.\[^{77}\] This covalent bonding is disturbed by interfaces such as the γ/γ grain boundary;\[^{78}\] pronounced covalent bonding was proposed for the symmetrical twin boundary, where asymmetrical twin boundary including antiphase boundary (APB) exhibits bonding similar to the pure γ-TiAl phase.

Regarding alloying, Wolf et al.\[^{89}\] calculated DOS of γ-TiAl containing V, Nb, Cr, and Mn. They concluded that V and Nb substituting Ti will cause only minor changes to DOS due to the similarities in the electronic structure between those TMs and Ti. More pronounced changes were obtained for Cr and Mn, which were mainly ascribed to their increased electronegativity. In contrast to this, a strongly modified DOS was obtained when the TM elements were substituted for Al. In particular, γ-Ti₂O₃AlMn exhibits DOS with Fermi level situated right in the middle of a pseudogap, hence suggesting well-separated bonding and antibonding states. Song et al.\[^{79}\] further uncovered hybridization Mn-3d, Ti-3d, and Al-3p electrons at the first nearest-neighbor distance in the case of Mn substituting for Al, hence strengthening the bonds, which can be finally correlated with Mn preferring the Al sublattice in γ-TiAl.

A peak in DOS at the Fermi level is often a sign of structural instability. Indeed, this is exhibited by DOS of β₆-Ti₅Al,\[^{90}\] partially smeared out by chemical disorder,\[^{50}\] and turns into a shallow local minimum when additionally Mo is alloyed.\[^{50}\] This behavior was interpreted as a combined stabilizing effect of Mo alloying and chemical disorder, in line with the diminishing dynamical instability of β₆-Ti₅Al.\[^{50}\]

\(\omega\) phase (Ti₅Al₄Nb) is structurally related to the β₆ phase, which is stabilized by Nb, and it can therefore appear in the microstructure of β-solidified TiAl alloys. Interestingly, atom probe tomography (APT) showed that the \(\omega\) phase is almost

Figure 6. a) Lattice parameters and b) formation energy of B19 and O phases as a function of Mo content. Experimental lattice parameters of B19–TiAl (red symbols) were reported by Abe et al.\[^{136}\] (full symbols, \(x_{Mo}=0\)) and Musi et al.\[^{160}\] (open symbols, \(x_{Mo}=3.25\) at.%).
completely depleted of Mo,[11] another known strong β-stabilizer present in TNM and TNM+ alloys.[16] Inspecting the charge density redistribution (Figure 7) in the $\omega_0$ phase, when one Nb atom is substituted by one Mo atom, the formation of directional Mo–Ti nearest-neighbor bonds is revealed with subsequent weakening of further-located Ti–Al(Nb) bonds. These changes in the electron density were identified as the electronic origins of the unfavorable presence of Mo in the $\omega_0$ phase and hence its depletion from the $\omega_0$ to the $\beta_o$ phase in multiphase microstructures.[11]

3. Material Properties

3.1. Lattice Parameters and Thermal Expansion

Electronic structure methods are well suited to provide alloying-related structural trends, that is, if volume increases or decreases with the addition of solute atoms or if one species causes larger (or smaller) lattice expansion than other. The ground-state structural properties are obtained straightforwardly for the ordered cubic as the lattice parameter is uniquely related to the equilibrium volume determined, for example, from Birch–Murnaghan’s equation of state (EOS).[80] The situation is somewhat more complex for lower symmetry structures. For example, for hexagonal $\alpha_h$ or tetragonal $\gamma$ structures, infinite pairs of $(a, c)$ lattice parameters correspond to the same volume; hence, before applying any EOS fit, one needs to find geometry with the minimum energy for a given volume. Obviously, the situation is one “layer” more complicated for the orthorhombic B19–TiAl structure. Those shortcomings can be easily overcome by applying a cell shape relaxation at a fixed volume followed by the EOS fitting or even applying a full relaxation.

Once compositional trends are dealt with, it becomes even more complicated. The SQS supercells essentially lead to breaking a macroscopic symmetry and typically a relaxation of, for example, a cubic structure leads to a noncubic-shaped simulation box. Several approaches can be applied in that case. First, one can enforce the macroscopic symmetry (i.e., fixing the cubic shape of the simulation box representing the β-TiAl structure) by relaxing only internal degrees of freedom (atomic positions) and subsequently applying the EOS fitting. Second, it is possible to apply a full relaxation, including a cell shape optimization, and then calculate the lattice parameter as a cubic root of the equivalent cubic equilibrium volume (i.e., $a_0 = \sqrt[3]{2V_0}$, when $V_0$ is the equilibrium volume per atom of a bcc-based β-structure). Finally, it is possible to simply average the lattice parameters after full relaxation, which destroys the cubic symmetry (i.e., $a_0 = (a + b + c)/3$).

The differences between those approaches are shown in Figure 8 for the Ti-rich compositions of β and $\beta_o$ phases. One can see that the three approaches provide relatively scattered results. This is likely related to the instability of the $\beta/\beta_o$ phases. Nevertheless, it is possible to conclude that 1) the disordered β phase yields $\approx 0.1$–0.2 Å larger lattice constant than its ordered counterpart $\beta_o$ and 2) that Mo leads to a slight decrease in the lattice parameter.[50] Abdoshahi et al.[64] discussed the spontaneous transformation of the $\beta_o \rightarrow \gamma$ phase, which is likely the reason why the structures with relaxed cell shape yield different β-equivalent lattice parameters than the calculation with a fixed cubic cell shape.

The differences between the various approaches are minute for stable structures (e.g., $\gamma$ or B19) but can be serious for unstable structures or systems with severe internal relaxations (such as the β phase[60]). Finally, let us note that the CPA-based results are not prone to those issues as they realize compositional variations by partial occupancies and keep the macroscopic symmetry of the system (e.g., β-TiAl remains an ideal bcc). However, the CPA method cannot reflect different local environments (e.g., clustering of atoms), which could lead to strong local distortions even in reality.

Although DFT is a ground-state theory, it can be used to estimate temperature-dependent material properties. One such example is temperature-dependent lattice parameters. The thermal expansion is obtained by conducting EOS fitting for each temperature independently, that is, instead of using 0 K energies $E_0(V)$ as input data; one uses Helmholtz free energies: (the sentence continues by Equation (5)).

![Figure 7. Charge redistribution upon Nb atom being replaced with Mo. Blue (yellow) shades represent charge accumulation (depletion). Adapted with permission.[11] Copyright 2017, Elsevier.](image)

![Figure 8. Mo-dependent lattice parameters calculated for Ti-rich compositions of disordered β and ordered $\beta_o$ phases using different approaches: fixed cubic cell shape (solid line) or fully relaxed cell shape (dashed and dashed-dotted lines). An experimentally measured lattice constant of the $\beta/\beta_o$ phase in the water-quenched state of the Ti–44Al–3Mo (at%) alloy reported by Musi et al.[60] is shown by the red symbol.](image)
\[ F(V, T) = E_0(V) - TS_{\text{mix}} + F_{\text{el}}(V, T) + F_{\text{vib}}(V, T) \\
+ F_{\text{ab}}(V, T) + \ldots , \]  

where \( F_{\text{el}}(V, T) \), \( F_{\text{vib}}(V, T) \), and \( F_{\text{ab}}(V, T) \) are free energy contributions corresponding to electronic, vibrational, and anharmonic excitations, respectively. Configurational entropy, \( S_{\text{mix}} \), is nonzero only for disordered or alloyed systems, where it is an important contribution at finite temperatures.

Similar to the 0 K lattice parameters, also here, the correspondence between the lattice parameter/cell shape and the volume is not unique for a noncubic system. An often used approximation is that the lattice parameter dependence on volume at 0 K is the same as that at finite temperature, that is, \( a(T, V) = a(0 K, V) \). This is a computationally acceptable approach that allows to include also vibrational free energy contributions, \( F_{\text{vib}} \), using only a few phonon calculations. This approach has been termed “ground-state optimized cell shape” (gs-cs) in the study by Holec et al., \(^{81}\) opposite the “temperature-optimized cell shape” (to-cs) approach. In the latter, all free energy contributions are calculated as functions of all-symmetry-nonequivalent lattice parameters, thus allowing for different cell shapes (e.g., \( c/a \) ratios) for the same volume as a function of temperature. Comparing those two approaches applied to \( \gamma\)-TiAl and \( \alpha_2\)-Ti₃Al phases yielded comparable results for the hexagonal \( \alpha_2 \) structure but significant differences for the tetragonal \( \gamma\)-TiAl. For example, the bulk modulus was predicted to soften with the increasing temperature by \( \approx 12\% \) between 0 and 770 K using the to-cs method. In comparison, the gs-cs approach resulted in (unrealistic) over 30% softening for the same temperature range. A general conclusion about the applicability of the computationally cheaper gs-cs method at this point is not possible as the gs-cs approach works well for the \( \alpha_2 \) phase but fails for the \( \gamma\)-TiAl. However, the reader should be aware of the deficiencies of the gs-cs method, which may lead to (unnoticed) false predictions.

The calculated thermal expansion coefficient for the \( a \) lattice constant of the \( \gamma \) and \( \alpha_2 \) phases compared with experimental data is shown in Figure 9. It demonstrates the predictive capability of \( ab \) initio calculation also for finite temperature properties. The discrepancies, especially in the case of the \( \gamma\)-TiAl phase, are likely to be caused by not exactly the stoichiometric composition of \( \gamma\)-TiAl, which additionally contains some alloying elements.

### 3.2. Elasticity

The calculation of the single elastic constants is done using either the stress–strain or the energy–strain method. The first one directly applies the linear relationship between stress and strain using Hooke’s law. This method is very robust and efficient, \(^{82}\) particularly when used with a set of linearly independent strains. \(^{83}\) It works for any crystal symmetry; when applied to disordered systems modeled using SQS supercells, it is desirable to project the resulting tensor of elastic constants onto the corresponding macroscopic crystal symmetry before further processing.\(^ {84}\)

The energy strain method is more widely applicable, also in cases when strain tensor is not available, for example, for the EMTO–CPA method, which is suitable for alloying. The applied specially designed strains increase the total energy, which is interpreted as the strain energy. Hence, it can be expressed as a second-order polynomial of the elastic constants. \(^{85}\) The advantage of this approach over the stress–strain method is that it allows estimation also of higher-order elastic constants \(^{85,86}\) and, when combined with the phonon calculations, can also predict temperature dependence of the elastic constants. \(^{87,88}\)

Of course, the energy–strain and stress–strain methods should, in theory, yield the same results, which they indeed do for well-behaved structures/systems and converged calculational parameters. This is demonstrated, for example, on an example of a low-symmetry (orthorhombic) B19–TiAl structure, where the largest discrepancy between those two methods is below 3\%. \(^{89}\) The single-crystal elastic properties calculated using DFT are typically within the 5–10% error bar with respect to the experimentally measured values; this is the case also for TiAl, as demonstrated for pure \( \gamma\)-TiAl and \( \alpha_2\)-Ti₃Al.\(^ {77,90}\)

The calculated single-crystal elastic constants can be used to calculate directional Young’s modulus. \(^{91}\) The thus obtained values using our own calculations are shown in Table 1, along with experimental moduli obtained from synchrotron measurements. \(^{92}\) Both experiment and theory yield \( E_{\{100\}} \approx E_{\{001\}} < E_{\{110\}} < E_{\{111\}} \). The same ranking was experimentally determined also by He et al. \(^{93}\)

We can now discuss the origin of numerical discrepancies between the actual values. Regarding experiments, the values of Erdely et al. \(^{92}\) were measured on a multiphase TNM alloy (overall...
composition Ti–43.5Al–4Nb–1Mo–0.1B, all in at.%); however, the actual composition of the γ phase was not determined. Moreover, the authors showed dependence on the processing parameters (rolling direction), suggesting that the values are not purely material properties but also depend on the microstructure. Using single-crystalline γ-Ti44Al26, He et al.\[23\] reported E\(_{111}\) > 200 GPa, that is, closer to the theoretical values. We note, however, that the exact composition of the measured material does not correspond to the ideal stoichiometric γ-TiAl. To be fair, one should also realize uncertainty on the theoretical side stemming mostly from the approximation of the exchange-correlation potential. Liu et al.\[22\] used a different flavor of GGA (PW91\[23\]) than in the present work (PBE\[22\]) but obtained a similar single-crystalline elastic constants C\(_{ij}\). On the contrary, Fu et al.\[90\] used LDA and obtained most of the elastic constants 5–10% stiffer, the exception being C\(_{12}\) (19% stiffer by LDA) and C\(_{66}\) (30% softer by LDA than GGA-PW91). In conclusion, although a direct comparison between experimental and calculated values of elastic constants is somewhat clumsy, the trends are well reproduced.

It is now desirable to use first-principle calculations to determine the alloying-related trends on the mechanical properties, which are crucial for structural materials. This is shown in Figure 10 where polycrystalline elastic moduli of γ-TiAl are presented as functions of Zr addition. Those correspond to the Voigt–Reuss–Hill averages representing microstructures with all-grain orientations having the same probability (i.e., no texture), yielding an elastically isotropic system. We have considered three scenarios where Zr replaces Al (Ti\(_{0.5}\)Al\(_{0.5}–\)xZrx), Ti (Ti\(_{0.5}–x\)ZrxAl\(_{0.5}\)), or both elements by the same amount (Ti\(_{0.5}–x/2\)Zrx/2Al\(_{0.5}–x/2\)Zrx/2). Clearly, alloying Zr into γ-TiAl reduces Young’s modulus, E, and shear modulus, G, whereas the bulk modulus, B, remains almost unaffected. Keeping in mind the discussion in Section 2.1, the direct substitution or Zr (group 4 element) on Al sublattice is not preferred as Zr exhibits a strong Ti preference. Therefore, we have considered also the situation with the Al:Ti equimolar ratio, but having all Zr on Ti sublattice, hence creating Ti\(_4\)Zr antisite defects. However, inspecting the points labeled with crosses in Figure 10, we can conclude that in this particular case, the Ti sublattice preference of Zr does not seem to impact the elastic response.

Surprisingly, there are fewer theoretical reports on mechanical properties available in the literature as one would expect. One of the oldest works deals with the impact of H on the mechanical properties of Ti\(_{1–x}\)Al\(_{x}\) alloys, showing that when both Al and H are present in the Ti matrix, valence charge depletes from certain planes, thus leading to enhanced local plasticity.\[94\] Wang et al.\[86\] conducted first-principle simulations of tensile tests of γ-TiAl doped with O, C, P, and S. They concluded that all those elements lead to a reduction in ideal tensile strength. Small concentrations of interstitial C in γ were recently reported not to be responsible for the ductilization of the γ phase.\[95\] Mo was reported to increase both bulk and shear moduli of the β phase.\[90\] Abdoshahi et al.\[96\] calculated that Mo increases bulk modulus, whereas it decreases Young’s modulus also for the α/α’-TiAl phase and concludes that Mo has a positive effect on the ductility of α/α’ and β phases.

Finally, let us note that by combining the quasiharmonic approximation with the elasticity calculations, it is possible to use ab initio calculations to predict temperature-dependent single-crystalline elastic constants, as demonstrated, for example, by Wang et al.\[97\] for several TiAl+X systems.

### 3.3. Bulk Diffusion

Segregation is a kinetic process, similar to ordering transformation, where, however, diffusion occurs typically on short lengths. At the atomistic level, Vineyard’s transition-state theory\[98\] is often used to estimate diffusion coefficients. The critical ingredients for this approach are migration barriers, which can be conveniently obtained using the (climbing image)-nudged elastic band (CNEB) method\[99\] and jump attempt frequencies.\[98\] Mishin et al.\[100\] studied self-diffusion of Al and Ti in γ-TiAl. They concluded that inside the tetragonal basal plane, Al diffuses faster than Ti for all concentrations from Ti\(_{0.64}\)Al\(_{0.36}\) to Ti\(_{0.36}\)Al\(_{0.64}\). In contrast to that, Ti is faster than Al perpendicular to the basal plane for Ti-rich compositions, whereas the opposite holds true for Al-rich compositions at 800 K. Epifano and Hug\[101\] used this approach to study the bulk diffusion of O, B, and H in γ-TiAl. They could show that all these species diffuse faster in the basal plane of γ-TiAl than across the tetragonal axis direction. Qualitatively, the same result was obtained also from Connétable\[102\] who, in addition to γ-TiAl, also studied H diffusion in hexagonal α2-Ti3Al andhcp Ti. Interestingly, the hexagonal structures exhibit faster diffusion along the hexagonal axis rather than in the basal plane. All those results were shown qualitatively and also quantitatively to agree with experiments.\[101,102\] Zhao et al.\[103\] showed that Nb increases migration barriers for bulk diffusion of O in γ-TiAl and, hence, Nb improves poor
oxidation resistance of the γ phase. For a comprehensive review on diffusion in the Ti–Al system, the reader is referred to publications of Mishin et al.\cite{103} or a more recent modeling-based review of Xing et al.\cite{104}

4. what About Microstructure?

4.1. Phase Preference for Alloying Elements

Structural alloys in general, and γ-TiAl-based alloys in particular, are characterized by a rich microstructure, which consists of several phases. The elemental distribution of individual atoms is not the same in all phases; it follows basic thermodynamic rules for the coexistence of phases. For example, inspecting the most simple situation, binary Ti–Al phase diagram,\cite{61} γ and α₂ phases coexist for an overall composition Ti₆₆Al₃₄. Not only does each phase have a different composition (apart from different crystal structures), but the actual composition is dependent on temperature as the phase boundaries are not straight vertical lines in the phase diagram. Obviously, solute atoms may exhibit different affinities for different phases, for example, Si strongly prefers α₂ phase over γ-TiAl\cite{10,106} or Mo partitions to the β₂ phase instead of the γ phase.\cite{58,64}

Determination of the exact composition of coexisting phases (which is, moreover, temperature and process dependent) is beyond what electronic structure calculations can provide. Nevertheless, a prediction of in which coexisting phase a solute element is more likely to segregate can be made. For example, Klein et al.\cite{10} studied phase formation in a multiphase TNM alloy bearing Si. The microstructure contains (at various stages) γ, α₂, β₂, and ω phases. They reported on first-principle calculations showing ΔE²<ω < ΔE²<γ < ΔE²<α₂, where Δ represents changes in formation energies upon including Si with respect to respective pristine phases. This means that the energetically most preferred location of Si is in the ω₂ phase, followed by the α₂ and the γ phases. The least favorable location of Si is in the β₂ phase, which is even slightly destabilized by Si. Using APT data, the Si concentrations in the individual phases were shown to follow cω < cα₂ < cγ < cβ₂, well in line with the theoretical predictions.\cite{10} A similar situation was also applied to Cr and Mo σ/γ-TiAl alloys.\cite{106} Both Cr and Mo are expected to be repelled from the growing γ phase into the β₂ phase. The same also holds for Cr and the σ phase once it appears, whereas Mo slightly stabilizes the σ phases (ΔEσ<0) and hence is expected to be present in both β₂ and σ phases. Those trends were corroborated by detailed APT data.\cite{106} Ye et al.\cite{107} also used formation energy change to discuss impact of V, Nb, Ta, Cr, Mo, W, and Mn on phase stability among Ti₂, β₂, and γ phases. Those predictions are consistent with other theoretical reports,\cite{108,109} which used similar methodology (separate treatment of both phases), as shown in other studies.\cite{10,106} Finally, all those predictions seem to be corroborated by existing literature APT data.\cite{10,106,109,110}

A multiscale/multimethod approach to element partitioning was demonstrated by Pham et al.\cite{111} The authors used ab initio calculations to parameterize free energies, which were subsequently implemented in a phase-field model. The method was applied to the Ti–6Al–4V (wt.%) alloy and the results clearly indicated enrichment of Ti β-grains with V, whereas Al partitioned into the α phase.

4.2. Segregation to Grain Boundaries

The characteristic feature of structural alloys is their polycrystalline nature. Grain boundaries are typically less dense and serve as natural segregation sites for surplus species. There have been numerous studies on grain boundary segregation, both experimental and theoretical, which gave rise to a whole subfield dealing with grain-boundary engineering.\cite{112,113} A common denominator of those studies is that they typically deal with 1) a single-phase system (e.g., fcc phase\cite{114}) and 2) a single species that forms the matrix (e.g., Al,\cite{115,116} Ti,\cite{117} or Fe\cite{118}).

A rather unusual attempt in this regard is the work of Gehringer et al.,\cite{12} who considered segregation to γ/γ-interface (i.e., in a two-component matrix) and γ/α₂ (i.e., two-component two-phase interface). Obviously, such interfaces appear in engineering multiphase TiAl alloys.\cite{103} The methodology turned out to be significantly more complicated than for single-species single-phase systems. Namely, the segregation energetics (i.e., a comparison of the energetically more convenient scenario–bulk or interface) must also include information about site preference, which may be different at the interface and in bulk. In the case of sublattice changes, additional antisite defects must be generated along the segregation pathway from bulk to the interface, introducing an additional barrier acting against segregation. Moreover, the lowered symmetry at the interface can lead to splitting sublattices into more symmetry nonequivalent sites than bulk, which all have to be taken into account separately. This innovative approach and detailed analysis have been recently presented in the study by Gehringer et al.\cite{12} Although the authors have concluded that the sublattice change is likely not an issue for the γ/γ and γ/α₂ interfaces in TiAl alloys, they may play an important design role for grain boundary engineering in other material systems. Finally, let us note that for a majority of the elements studied in the study by Gehringer et al.,\cite{12} (3d, 4d, and 5d TMs and Si), the phase partitioning overrules any grain boundary segregation for γ/α₂ interfaces. Thermodynamic driving forces for segregation into the twist γ/γ interfaces were shown to be very low, probably related to those defects’ tight character. This is consistent with the APT data, which usually do not show any accumulation of the solvent atoms at the
γ/α₂ interfaces but instead a gradual increase in concentration toward the preferred phase. In this respect, an interesting result is a slight tendency to segregate of middle-TM elements into the γ/γ twist interfaces. Although they increase the critical tensile strength of the interface upon segregation, they lead to softening the elastic constants and thereby to a slight lowering of fracture toughness $K_{IC}$. APBs and stacking faults (SFs) are important defects in γ-TiAl, which are closely related to the dislocation core structure and hence mechanical properties of the γ phase. SFs in γ-TiAl have been addressed in the literature using DFT, including the alloying impact on the SF energies. APBs represent a special case of boundaries that can appear in ordered compounds. APB energies in γ-TiAl were numerously reported in the literature, e.g., see other studies. Moreover, Asta and Quong showed that APB energies are compositionally dependent (i.e., influenced by the local off stoichiometry) and significantly reduce with increasing temperature, thereby bringing the electronic structure predictions in agreement with experimental data.

4.3. Toward Phase Diagrams

Phase diagrams play an indisputable role in the development and design of an alloy. They allow for fine tuning the microstructure, which in the end controls the macroscopic material properties. First-principles calculations are well suited in predicting alloying of individual (bulk) phases, but their assembly into a microstructural model is beyond the reach of the electronic structure calculations. Mesoscale and/or semiempirical homogenization schemes are needed for predicting mechanical response in such cases. Nonetheless, those need input information about phase compositions and fractions, which can be obtained from phase diagrams. It is therefore of immense interest to explore the potential for ab initio calculations for their construction.

The advantage of first-principles calculations is that they can provide unbiased and large data via high-throughput approaches and/or using large material databases such as Materials Project or NOMAD Lab. The two major limiting factors are 1) description of solid solutions and 2) obtaining accurate temperature-dependent free energies. SQS and CPA approaches for addressing the former issue were briefly introduced in Section 3.1. The latter is an active field of research, whose detailed description is beyond the scope of the present article.

An initial step for obtaining the thermodynamic description is the calculation of 0 K mixing enthalpies. A handy tool to do so is the ATAT. Ghosh et al. and Chakraborty et al. demonstrated that the CE constructed using the ATAT package is capable of predicting correct ground states of the fcc-based structures in the Ti–Al binary system. This is also what we show using our own VASP calculations in Figure 11. Those convex hulls are qualitatively in agreement with earlier calculations by Asta et al. using LDA exchange-correlation functional instead of GGA used in other studies and here.

Once the CE is also extended to other crystal symmetries, it is possible to use the cluster variational method (CVM) together with Monte Carlo simulations, to construct the phase diagram. This was demonstrated for the Ti-rich part of the Ti–Al binary system by considering CEs of fcc and hcp structures (hence, obviously, excluding the hcp→bcc transformation of Ti). Those phase diagrams based on the CVM method are qualitatively correct, but they tend to overestimate transition temperatures by omitting vibrational contributions to the free energy. Onodera et al. showed that by parametrizing the temperature dependence of the effective cluster interactions using experimental data for pure elements, it is possible to use the CVM method to construct a phase diagram which agrees quantitatively with experimental data. Such treatment, however, goes beyond electronic structure-based methods. Nevertheless, Davey et al. recently demonstrated on an example of the Ni–Al binary system a successful approach for calculating the free energies fully by ab initio-based thermodynamic expansions and consequently constructing a binary phase diagram. Although this is at present still a calculationally costly approach, the emergence of novel tools, such as pycalpad, paves the path for practical utilization of electronic structure methods for predicting phase diagrams.

5. Outlook and Future Developments

With more computational power, more data can be generated and hence we are now experiencing a dawn of new approaches. Data mining combined with machine learning is likely to provide correlation between various, sometimes seemingly unrelated, material properties. In here, electronic structure calculations play and will play an important role to provide unbiased and coherent data across large sets of material systems.

The increasing computational power also allows for studying even larger and more complicated (structurally complex) systems. The focus even in electronic structure calculation shifts towards defect engineering, for example, grain boundary segregation. In this respect, it will likely not be the ab initio method alone but a combination with other techniques which will allow for studying really extended defects. This involves mainly interconnecting electronic structure methods with atomistic...
simulations. A direct interface involving both methods simultaneously is the QM/MM approach. Another very promising and increasingly more popular method is using ab initio to provide source data for constructing MLIPs which are subsequently used in simulations involving thousands to millions of atoms.

Finally, we envision that the combination of available computational power and movement toward open data sharing will allow efficient and accurate electronic structure methods-based tuning of phase diagrams.

6. Conclusion

In this article, we reviewed applications of electronic structure calculations, aiming on revealing alloying-related trends in structural and mechanical properties. The unifying theme were intermetallic γ-TiAl-based lightweight alloys. We started with constructing crystalline models by examining site preference for alloying elements. The site preference strongly depends not only on the element and the phase, but also on the position in the microstructure, for example, bulk versus near grain boundary. Energy landscapes help in exploring phase transformations; also here, the alloying impact on transformation barriers can be estimated. Next we demonstrated estimation of lattice parameters and single-crystalline elastic properties. The latter serves as input for continuum-based homogenization techniques which finally predict mechanical properties that can be compared with experimental values strongly influenced by the actual microstructure. Importantly, the state-of-the-art ab initio modeling allows for predictions at finite temperatures. The selected examples demonstrated capabilities of electronic structure calculations in predicting unbiased materials data, which can on the one hand provide interpretation for experimental observations and on the other hand guide experiments toward efficiently exploring new material systems.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

alloys, density functional theory, electronic structure methods, mechanical properties, segregations, structural properties, titanium aluminides

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