A First-Principles Approach to Modeling Alloy Phase Equilibria

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This paper presents a brief overview of recent developments in the application of first-principles calculations to the study of bulk and interfacial thermodynamic properties and phase equilibria in alloys. Among the applications discussed are calculations of: bulk thermodynamic properties, phase boundaries, interfacial free energies, and precipitate morphologies. The article concludes by highlighting some further recent developments that are likely to lead to increasing applications of these modeling techniques.

INTRODUCTION

In recent decades, substantial progress has been made toward parameter-free modeling of phase equilibria in metallic alloys. Fundamental knowledge of the microscopic factors governing alloy phase stability has increased greatly as a result of first-principles calculations based upon theories of quantum physics and statistical mechanics. Recent work has demonstrated substantial quantitative improvements in the accuracy of alloy phase diagrams calculated from first principles. Also, ab-initio methods have been extended recently to calculate both bulk and interfacial thermodynamic properties, which are being used to improve the predictive capabilities of microstructural evolution simulations in alloys. The development of a predictive first-principles framework for the calculation of alloy-phase stability has benefited from enormous increases in computing power coupled with significant advances in the accuracy and efficiency of computational methods. With these recent improvements in scope and quantitative accuracy, ab-initio methods are becoming a significant tool for alloy development. This article presents a brief overview of these computational methods through a review of recent applications to the modeling of precipitation thermodynamics in Al(Sc) alloys. These examples are intended to represent the current state of the art in applications of first-principles modeling to the calculation of phase boundaries in binary and multicomponent alloys, heterogeneous interfacial free energies, and equilibrium precipitate morphologies. Far more extensive reviews of first-principles alloy-thermodynamic computational methods can be found in References 1–8; this article only highlights a few recent developments in this field.

Because of their high specific strengths, aluminum-rich Al-Sc alloys are increasingly being considered for applications at high homologous temperatures. Scandium, which provides the greatest increase in strength, per atomic percent, of any alloying addition in Al, is only slightly more dense (about 11 percent) than aluminum itself. That strengthening effect is attributed to the small (5–30 nm) coherent AlSc precipitates that form during the ageing of supersaturated Al(Sc) solid solutions in the temperature range of 300–350°C. The AlSc phase forms in the face centered cubic (fcc)-based L12 crystal structure.

BULK ALLOY THERMODYNAMIC PROPERTIES

The starting point for a first-principles calculation of phase equilibria is an accurate quantum-mechanical calculation of bulk-alloy energetics. Figure 1 shows the results of such first-principles calculations for the formation enthalpies (ΔH) of observed intermetallic compounds in the Al-Sc system. The dark filled symbols in Figure 1 represent the results of first-principles calculations performed within the framework of electronic density-functional theory (details of the calculations can be found in Reference 18). Open symbols in Figure 1 correspond to measured data from high-temperature (diamonds) and reaction-drop (circles) calorimetry. Foreach compound, the measured and calculated values are found to agree to within ten percent (5 kJ/mole) with the level of agreement between experiment and theory comparable to that between independent calorimetry measurements. Similar accuracy has been demonstrated in first-principles calculations of AH for a wide range of metallic alloy systems (see, for example, References 1–3). In the absence of available calorimetry data, first-principles calculations can be employed readily to calculate compound formation enthalpies to augment alloy thermodynamic databases required in Calphad “computational thermodynamic” modeling of phase diagrams. By combining quantum mechanics with computational thermodynamics, first-principles calculations are finding application in alloy design.

In addition to providing accurate total energies, density-functional theory has been widely used as the basis for first-principles calculations of bulk and defect alloy thermodynamic properties at finite temperatures. A significant challenge associated with such calculations is the accurate calculation of both the energy and entropy contributions to alloy free energies. For the aluminum-rich solid-solution phase in Al-Sc, the equilibrium solid-solubility of scandium is known to be extremely low, less than a few tenths of an atomic percent at the eutectic temperature of 660°C. Similarly, the equilibrium AlSc phase field is extremely narrow, and the phase is known to remain highly ordered up to the melting point. Therefore, equilibrium solution-thermodynamic properties of the Al(Sc) and AlSc phases can be described accurately by ideal-solution...
the Al$_3$Sc phase is found to be strongly
the vibrational entropy of formation of
motion versus ordered Al$_3$Sc. Specifically,
was traced to a difference in sign be-
limit. The origin of this effect
sured scandium solid-solubility
boundary at the maximum mea-
aging to a 450 K decrease in calcu-
for scandium in aluminum, lead-
calculated solid-solubility limits
for a 27-fold enhancement of the
vibrational entropy accounted
measurements. 11,24–26 The first-
limits derived from resistivity
results of such a calculation, taken
ents required as input. The re-
numbers of the alloy constitu-
phase-boundaries for alumi-
results of such calculations,
ment factors influencing phase equilib-
insight into the microscopic fac-
the calculations provide detailed
are modeled from first principles,
level of accuracy displayed in
down to temperatures up to the mea-
quired solid solubility limits from resistivity measurements. 11,24–26 The first-
principles calculated phase boundaries agree to within 50 K
of experimental measurements to
to a weakening of these bonds and an
distant Al-Al nearest-neighbors, lead-
gives rise to perturbations in charge (see
charge density shows characteristic long-
ated scandium are colored red (corresponding to {111} facets).
atoms with four NNN scandium are colored green
next-nearest
state in an aluminum matrix, as predicted from first-principles
ab-initio studies of alloy thermodynamic
properties to date 25–39 (a very recent re-
view is given by van de Walle and
The example in Figure 2 dem-
strates the first-principles cal-
ulation of phase boundaries between
phases with di-
ict due to vibrations.
It is,
important to stress that comparable accuracy has been
demonstrated in several first-
principles calculations for alloys
with concentrated compositions.
Specifically, the cluster expa-
sion framework 2–4,42 has found
application in the first-prin-
ciples calculation of phase dia-
grams for metal and semi-
ceramic systems. 6,44 The method
provides a formalism for expres-
ging the energy of different atomic
arrangements on an underlying
lattice framework in terms of an
body cluster interaction parame-
ters. These parameters are de-
erived from electronic perturbation
theories 1.3,4–41 or by fitting to re-
results of first-principles calcula-
tions of alloy energetics 2–4.

INTERFACIAL THERMODYNAMIC PROPERTIES

Once an accurate parameterization of the
energy has been derived, the cluster expansion provides a rapid
method for calculating energies of alloy
phases with arbitrary degrees of chemi-
cal short- and long-range order. Specifi-
cally, the method provides a first-prin-
The first-principles basis for efficient Monte-Carlo simulations that permit the calculation of configurational free energies, short-range order, and phase diagrams for alloys with concentrated compositions. Although applications of the first-principles cluster expansion framework are too numerous to review in the present article, References 2–4, 43, and 44 provide examples and further details. Following are examples of recent applications of the approach to calculating interfacial free energies 56-57 and modeling coherent precipitate morphologies 53-54.

Figure 4 displays the equilibrium shape of an Al\textsubscript{3}Sc precipitate obtained from Monte-Carlo simulations at a temperature of 600 K.\textsuperscript{58} These simulations were based upon a cluster-expansion parameterization of the vibrational free energies\textsuperscript{59}, resulting in a thermodynamic model consistent with the results shown in Figure 2. The simulation conditions leading to the structure shown in Figure 4 were chosen to produce a precipitate with a diameter of roughly 7 nm. Specifically, simulations were conducted with fixed numbers of aluminum and scandium atoms, with an overall composition beyond the equilibrium solvus boundary. The simulations were initiated with a random arrangement of aluminum and scandium atoms on the sites of an fcc lattice, and, after a prolonged equilibration period, the Al\textsubscript{3}Sc precipitate nucleated, grew, and finally equilibrated to the shape shown in Figure 4.

The simulation study was motivated by a very recent detailed transmission-electron-microscopy study of Al\textsubscript{3}Sc precipitate morphologies performed by Marquis and Seidman.\textsuperscript{13} In Al-0.3 wt.% scandium alloys aged between 300°C and 400°C, the authors clearly observed faceted morphologies for coherent precipitates ranging between 5 nm and 10 nm in diameter. Because facets were observed on 100, 111, and 110 precipitate faces in well-annealed samples, the equilibrium crystal shape for these small Al\textsubscript{3}Sc precipitates was concluded to be a Great Rhombicuboctahedron.\textsuperscript{10} In more dilute Al-0.1 wt.% scandium alloys, similar heat treatments were observed to lead to complex cauliflower precipitate morphologies (observed also by Novotny and Ardell\textsuperscript{9}), interpreted as the result of growth instabilities associated with the lower supersaturation levels.\textsuperscript{15}

The first-principles simulations leading to Figure 4 were a basis for establishing the equilibrium crystal shapes of nanometer-scale precipitates in Al-Sc to further validate these interpretations of the experimental observations. The simulation results represented in Figure 4 predict an equilibrium precipitate morphology that is clearly faceted on 100 planes. Furthermore, the rounding of cube corners and edges in the simulated precipitate shapes can be interpreted as reflecting a tendency towards faceting on 110 and 111 planes as well. These simulation results clearly support the interpretation\textsuperscript{15} that equilibrium crystal shapes of 5-10 nm Al\textsubscript{3}Sc precipitates are highly faceted. Furthermore, these first-principles calculations confirm continuum-model predictions\textsuperscript{29} that the morphologies of Al\textsubscript{3}Sc precipitates with diameters in the range of 5-10 nm are negligibly affected by anisotropies in the elastic strain energy of precipitate and matrix phases. Rather, the equilibrium shapes of these small precipitates are found to be a reflection of the anisotropy of Al/Al\textsubscript{3}Sc hetero-phase interfacial free energies.

Figure 5 plots the temperature dependence of first-principles calculated excess free energies (\(\gamma\)) for coherent Al/Al\textsubscript{3}Sc interfaces with 100 and 111 crystallographic orientations. These results represent an extension of previous work\textsuperscript{60,61} devoted to the calculation of interfacial free energies in this system. Figure 5 exceeds previous work by incorporating vibrational entropy in the calculation of excess free energies\textsuperscript{38} (using the same first-principles free energy model leading to the results in Figure 4). The calculated temperature dependence is found to be appreciable between 400–800 K with 100 and 111 free energies decreasing by roughly 25 percent over this temperature range. From the standpoint of precipitate morphology, the important feature of the curves shown in Figure 5 is the appreciable anisotropy between 100 and 111 interfacial free energies. Using previously published, first-principles-calculated zero-temperature interfacial energies\textsuperscript{80} in a Wulff construction, Marquis and Seidman\textsuperscript{13} established that the degree of anisotropy is sufficient to lead to faceting of the type observed experimentally. These authors also considered the magnitude of the first-principles calculated values of \(\gamma\) in light of results obtained for coarsening kinetics, finding reasonable agreement between theoretical and measured coarsening rate constants in this system.

**TERNARY SYSTEM APPLICATIONS**

To date, first-principles calculations of alloy phase equilibria have been applied primarily to binary systems, with relatively few such calculations performed for ternary systems.\textsuperscript{62-73} Because technologically relevant alloys generally possess many more than two components, there is considerable motivation to extend the range of applicability of first-principles methods to multicomponent systems. At present, accurate first-principles calculations of phase diagrams for concentrated ternary systems remain a significant challenge, with applications to systems with four or more components largely intractable. However, for systems such as Al-Sc, in which the equilibrium defect concentrations are dilute, the first-principles computational framework described in the previous paragraph can be readily generalized to multicomponent systems, as detailed in Reference 74.

For example, consider the partitioning of magnesium in dilute two-phase Al-Sc-Mg alloys. Experimentally, it has been determined that magnesium ternary additions partition strongly to the...
Al phase in two-phase Al-AlSc alloys. Figure 6 shows the results of a first-principles calculation of the magnesium solute distribution across a (100) Al-AlSc interface in two-phase, Al-rich, AlSc-Mg alloys. The plotted symbols, which correspond to calculated composition profiles across the interface, clearly show the magnesium partitioning to the aluminum phase, in agreement with experimental observations. Additionally, these calculations suggest that magnesium is enhanced at the interface. In other words, equilibrium segregation of magnesium solute to the interfacial boundary is predicted, leading a non-interfacial intercalation excess concentration (adsorption) of this ternary alloying species. The magnesium atoms are found to prefer crystallographic positions that are second-neighbors to interface scandinium atoms. The calculations leading to the results in Figure 6 were based on the formalism of dilute solution thermodynamics as described in Reference 74. Due to the relatively concentrated compositions of magnesium near the interface, the approach is not expected to be quantitatively valid. However, the methodology clearly provides valuable insight into trends related to phase partitioning and interface adsorption, important information from an alloy-design perspective that is often difficult to probe experimentally.

CONCLUSIONS

In a recent article, Chen et al.87 discuss a strategy for linking the types of first-principles methods discussed in this article with higher length-scale phase-field models of microstructural evolution. This combination of atomic and mesoscale models provides a novel hierarchical multi-scale framework for predictive modeling of materials evolution accompanying solid-state phase transformations occurring in the processing of alloys. An important recent development is the formulation of a cluster-expansion framework for modeling in a consistent first-principles framework both thermodynamic and kinetic properties of alloys.77 Specifically, van der Ven et al.77 recently described how first-principles calculations of migration energies for vacancy diffusion can be incorporated within a cluster-expansion model of alloy thermodynamics, forming the basis for ab-initio kinetic Monte Carlo studies of diffusion and ordering kinetics in alloys. This approach should prove to be of practical value in interpreting kinetic databases employed in the modeling of solid-state phase transformations in alloys. Also, an effort is underway to automate the first-principles methods described above for the calculation of alloy phase diagrams.78

It is increasingly recognized that first-principles computational techniques, when combined with complementary modeling methods, including computational thermodynamics and meso-scale models of microstructure evolution, can play a role in reducing the time and cost associated with the process of materials development. With continued developments in accuracy, computational power, and automation, the first-principles framework outlined in this article is anticipated to be applied more and more as a computational modeling tool in the science and engineering of alloys.

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