ORNL/TM-2019/1230
CRADA/NFE-17-06814

High Performance Computing for Phase Predictions for Multi – Component Alloy Systems

Final CRADA Report

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February 28, 2019

OAK RIDGE NATIONAL LABORATORY
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Program: HPC4Mfg
Division: Materials Science & Technology

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Date Published: July 2019

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

1. ABSTRACT

The goal of this work is to establish important alloy new data from rigorous, first-principles-based computational approaches, for systems that presently lack critical data. The focus is on lightweight alloys due to their importance in energy-efficient applications for transportation and other areas, particularly for alloy compositions such as Al-Li-Ti where existing data is limited. By providing input on this class of compositions, we seek to significantly reduce the effort, expense and energy of experimental explorations of these materials.

2. STATEMENT OF OBJECTIVES

The primary objective is to computationally examine the feasibility of forming favorable, lightweight alloys that may have unique properties, in composition spaces that are relatively unexplored. The project put a particular focus on alloys based on significant amounts of the three elements Al, Li, and Ti, where the low melting and boiling point of Li, combined with the high melting point of Ti, makes it unfeasible to form an Al-Li-Ti liquid suitable for casting. Nevertheless, there are approaches for making such alloys, but the cost, energy and effort for making such materials, combined with a large space of potential alloy compositions, make a computational approach for screening such alloys an important step in this process. This overall objective requires efforts in database construction and exploration, high-throughput calculations, and simulations of phase evolution in these materials.

As part of this work, we became aware of recent experimental reports that indicate that related alloys (namely, Al-Li-Ti-Sc-Mg) may form single phases with interesting properties (high hardness), when processed directly [1]. This work capitalized on recent databases of high-throughput calculations [2,3]. The ORNL participants had prior work in identifying potential single-phase high entropy alloys [4-6] from these databases, and combining these with Monte Carlo (MC) simulations to predict phase evolution in five-component alloys [7]. In particular, the ORNL work did not rely upon experimental input, making this useful for exploration of novel alloys in the present CRADA. The relevance of using high throughput computational approaches for identifying potential alloys for further synthesis and for potential manufacturing applications made this an ideal for an HPC4Mfg project.

Based upon these main goals and prior work, the following objectives were pursued, in close discussion between ORNL and Arconic Inc.:

Database construction (Task 1 of proposal): A database of binary density functional theory (DFT) calculations was constructed, and validated by comparison with available experimental results. These calculations are the basis for the Monte Carlo calculations, and also provide important checks on both the high throughput calculations and the Monte Carlo simulations. This database included binary calculations and convex hulls of pairs of elements including Al, Li, Ti, Mg, and Cu. An important result was that, for Li-Ti, where experimental data is most sparse, high throughput calculations showed (in agreement with existing experimental data [8]) that there is essentially no solubility of Li and Ti in any crystal structure. The lowest energies of relevant compound phases are given in Table 1. The element Sc was included due to its relevance from the experimental report [1]. This table forms the basis for interactions used in the MC code. Based upon the examination of this table, interactions of Al, Mg, and Li with Sc and Ti are very similar.

	Mg	**Al**	**Sc**	**Ti**	**Cu**	**Li**
Mg	0	-33	2	20	-147	-64
Al	-33	0	-444	-428	-224	-190
Sc	2	-444	0	38	-284	94
Ti	20	-428	38	0	-147	99
Cu	-147	-224	-284	-147	0	-72
Li	-64	-190	94	99	-72	0

Table 1. Lowest energies of formation (in units of meV/atom) for relevant pairs of elements, as identified through high-throughput density functional calculations.

Monte Carlo tests for known systems (Task 2 of proposal): We used the MC code, utilizing the binary interactions by DFT calculations (Task 1), to calculate the phase stability of known alloys. The work focused on the Al-Ti system, particularly near the $AlTi_3$ composition, where the composition-dependent ordering temperature in the Ti hexagonal close-packed (HCP) phase is well documented [9]. The results for the Al-Ti system were in reasonable agreement with experiment. The Al-Cu system at low Cu contents were also tried; however, the MC results were not in good agreement, due to the fact that the Al_2Cu phase, which is stable to temperatures above the Al-Cu eutectic (548 °C), has a crystal structure that cannot be described as ordering on a face-centered cubic (FCC) lattice (the crystal structure of Al). The importance of 2nd neighbor interactions on the ordering and interfacial energies was identified as a critical issue for full ordering of the binary systems.

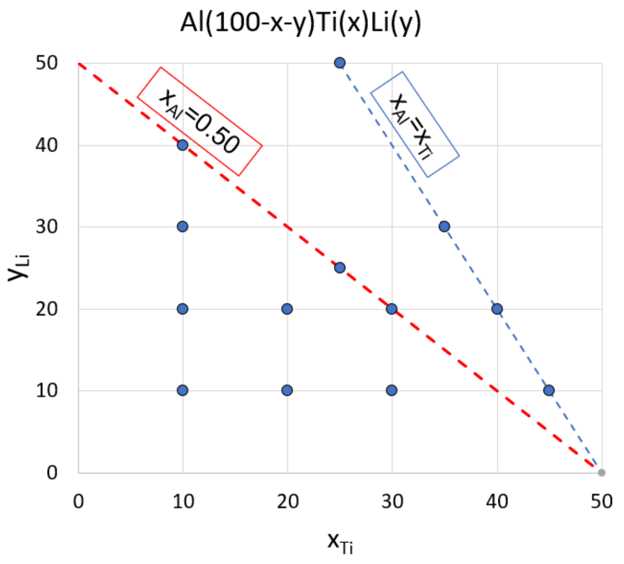

Figure 1. Compositions selected for the $Al_{100-x-y}Ti_xLi_y$ Monte Carlo simulations. Each simulated composition is denoted by a blue dot. Red line indicates the Al-50% line, while the blue line indicates the line for equal atomic fractions of Al and Ti.

Monte Carlo simulation of ternary and higher compositions (Tasks 3 and 4 of proposal): The MC code was applied to a series of complex alloys where little experimental data is available, including Al-Ti-Li and more complex alloys based upon this (including Al-Ti-Li-Mg and Al-Ti-Li-Mg-Sc). The phase stability as a function of temperature and composition was examined, particularly looking for evidence of Al-Ti-Li coexistence. Some of the compositions considered are identified in Figure 1.

Ab initio study of Al-based solid solutions (Task 5 of proposal): A critical issue associated with the enthalpy matrix (Table 1) for use in the Monte Carlo studies is that this does not provide critical information on the energies of disordered alloys, which is important for understanding the phase stability and evolution of the alloys. There is presently no high throughput database such as those that exist for ordered compounds [2,3]. Therefore, we initiated a high-throughput calculation of such disordered compounds in the FCC structure of Al, using both large unit cell structures and using the Coherent Potential Approximation (CPA) [10]. For Al-Ti, this demonstrated that the random solid solution has a low enthalpy (i.e, strongly negative), indicating that Al and Ti can favorably mix in this structure.

3. BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

The goals of this project were to advance the discovery of light-weight alloys, which can contribute to innovative technologies that reduce energy usage. This includes a reduced cost and energy required to generate necessary knowledge for alloys that are intrinsically hard to manufacture. In particular, this project generated significant data, and utilized existing data, in combination with high performance computing, in order to understand the possible of manufacturing new alloy compositions, that may contribute (for example) to new alloys for vehicles.

4. TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

4.1 *Database construction*:

A key initial deliverable is a database of first-principles calculations of energies of relevant binaries, and a comparison with known thermodynamic information. This database was constructed, using existing data from the literature, and using data from the AFLOW database [3]. As required, this was supplemented with our own calculations. A summary for the Al-Ti, Al-Li, and Li-Ti binaries are presented in Figure 2. From this figure, we see a close correspondence between the points on the computed convex hull (top) and the low-temperature observed structures. Note that the lowest formation enthalpies shown in Figure 2 are used to inform Table 1, and are used in the Monte Carlo simulations discussed below. Al forms very stable compounds with Li and Ti, persisting to high temperatures (above 1400 °C for ordered phases of Al-Ti, and above 700 °C for Al-Li). In contrast, calculations show that Li and Ti have no favorable compounds (all mixing enthalpies are positive). There is limited experimental data; what exists indicates that there is no mutual solubility in the solid or liquid phases. The Li-Ti phase diagram in Figure 2 indicates the difficulties in studying Li-Ti-based compounds: Li melts at 181 °C and boils at 1327 °C, while Ti melts at

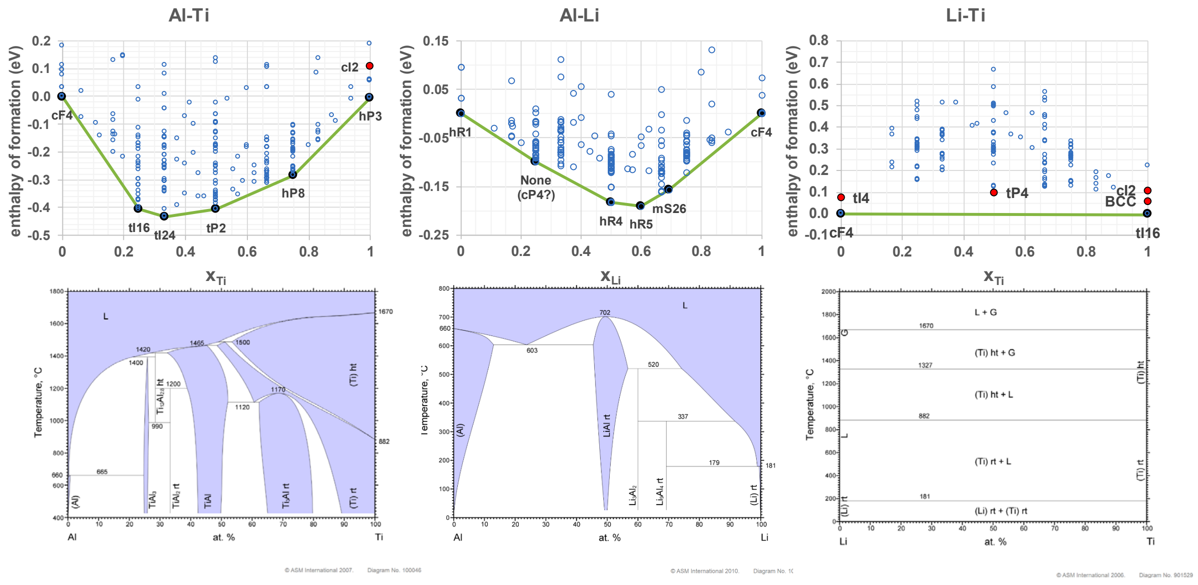

Figure 2. Comparison of high-throughput calculations with phase diagram information for Al-Ti, Al-Li and Li-Ti binaries. (Top) Calculated enthalpy of formation vs. composition for ~150 possible crystal structures for each binary. Green line shows convex hull that indicates most likely composition ranges at low temperatures, with most relevant crystal structures indicated. (Bottom) Corresponding phase diagrams, from the ASM International data, based on existing literature.

1670 °C. Thus, casting such compounds from the melt is infeasible. The database includes enthalpies of formation for each potential crystal structure (each data point in the top graphs of Figure 2), for each pair of elements in Table 1.

4.2 Monte Carlo tests for known systems:

To test the use of Monte Carlo simulations against known results, a number of tests for different systems was performed. In particular, the ordering transition in Al-Ti near x_{Ti}=75 at-% was particularly studied. Thermodynamic results from the simulations, shown in Figure 3, indicate a sharp heat capacity peak and enthalpy change associated with this ordering. The dimensionless "reduced temperature" is defined by $T_{red}=k_B T/J_{Al\text{-}Ti}$, where $J_{Al\text{-}Ti}$ is an effective near-neighbor coupling. If $J_{Al\text{-}Ti}$ is chosen to be the value given by the corresponding matrix element in Table 1, then the reported transition temperature is reproduced reasonably accurately. If, instead, the theoretical energy associated with the low-temperature ordered phase (designated as hP8 in Figure 2) is chosen, the transition temperature is underestimated. This is an issue that must be recognized associated with the predictions, and the approximations made to perform the Monte Carlo work. However, the goal of this project is not to accurately predict phase transition temperatures, but rather to explore potential alloy compositions. For this purpose, these tests were deemed acceptable.

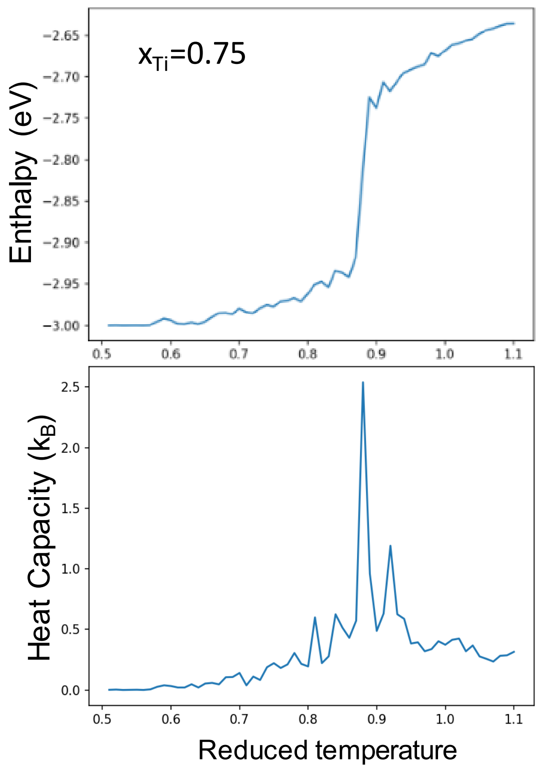

Figure 3. Monte Carlo simulated thermodynamics of $Al_{25}Ti_{75}$ through the ordering transition (near 1170 °C in the phase diagram shown in Figure 2).

However, the simulations revealed an important potential issue with the simulations. The low temperature of $AlTi_3$ is shown in the left-hand side of Figure 4. The arrangement of Al atoms is characterized by an alternating "zig-zag" structure. While the simulated structure (right-hand side of Figure 4) has local structures very similar to this, the chains of Al atoms are disordered. This is because within the near-neighbor approximation in the original MC simulations, there is no interaction between the chains, as changes in bonding only occur at 2nd nearest neighbors and beyond. This ultimately led us to add 2nd nearest neighbor interactions in later studies, which were chosen such as to preserve the energy of the low-temperature structure, but which increased ordering. This also had the effect of increasing transition temperatures, due to the thermodynamic penalty associated with the high-temperature, less ordered structures.

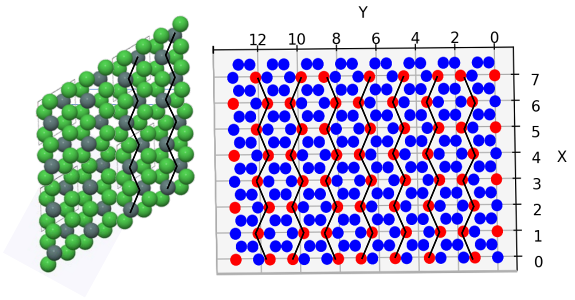

Figure 4. (Left) Ideal low temperature structure of $AlTi_3$. Note alternating "zig-zag" pattern of Al atoms. (Right) Simulated Monte Carlo structure with only near-neighbor interactions. The "zig-zag" structure is not ordered, due to the lack of longer-range interactions.

4.3 Monte Carlo simulation of ternary and higher compositions

The primary goal of the project was to explore the possibility of exploring composition space using a combination of high-throughput first-principles calculations and MC simulations. The primary focus was on the Al-Li-Ti system, including compositions shown in Figure 1. The primary focus is on Al-rich compositions, due to expense and weight considerations.

One composition that was initially examined was $Al_{60}Ti_{20}Li_{20}$, which served for a number of tests, including the role of 2^{nd} nearest neighbor interactions, motivated by our early MC work on Al-Ti (see Figure 3 and Figure 4, along with associated discussion). The next-nearest neighbor interactions were chosen to penalize different atom types on 2^{nd} nearest neighbor sites, which does not affect the energies of the ordered structures considered here, but encouraged a more ordered structure. For pure Al-Ti, even a small interaction prevented the unphysical disorder demonstrated in Figure 4. For the $Al_{60}Ti_{20}Li_{20}$ composition, the low-temperature structure for a next-nearest neighbor interaction of 0.010 eV is shown in Figure 5. Monte Carlo simulations result in a low-temperature mixture of AlTi, Al_3Ti, and AlLi phases, for all choices of next-nearest neighbor interactions of the chosen form. Given what is known from experimental phase diagrams and the high-throughput binary calculations shown in Figure 2. The calculations in Figure 2, and a comparison of the mixing enthalpy matrix of Table 1, shows that Al mixes more favorably with Ti than with Li; thus, in all of our simulations, there is a tendency to form Al-rich phases with Ti rather than Li. In the case of $Al_{60}Ti_{20}Li_{20}$, this results in the additional Al forming the Al_3Ti phase, rather than forming an Al_3Li phase. This general trend follows most of the calculations.

While the strength of the next-nearest neighbor interaction did not affect the low-temperature structure, having a non-zero value was important for forming an ordered phase, and the value affected the transformation temperatures. This is illustrated in Figure 6, which shows the low-temperature structure and the heat capacity calculated during the simulated cooling of the samples. As can be seen, the stronger interactions result in a more ordered structure. In the absence of a next-nearest neighbor interaction, the low-T structures (near 100 K) is significantly disordered, and no peak in the heat capacity C_V is observed

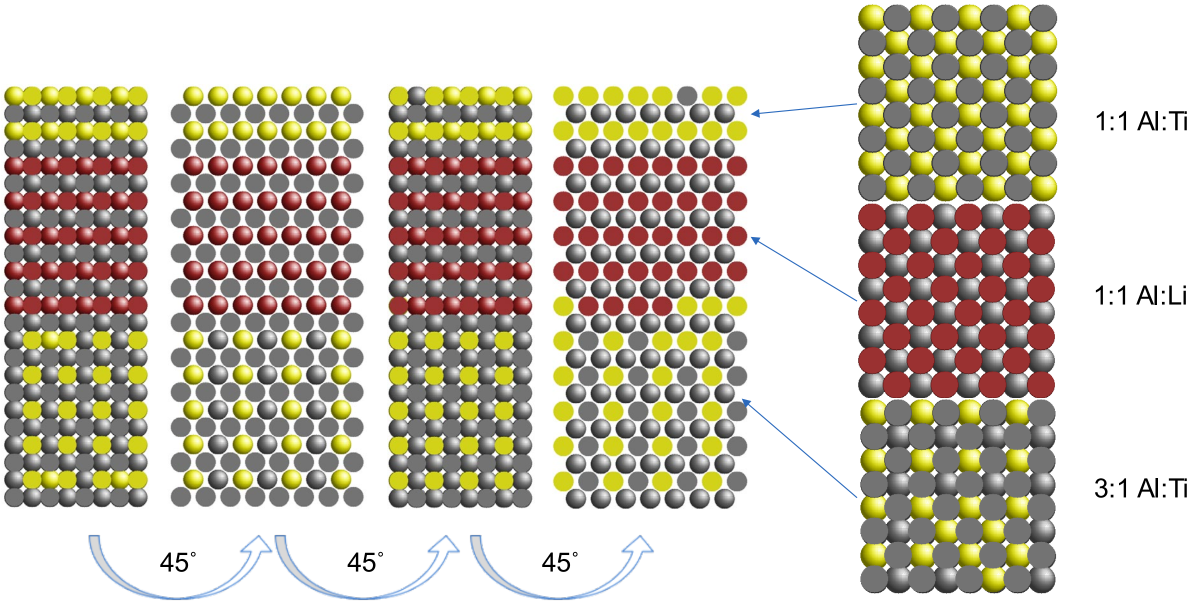

Figure 5. Monte Carlo result for low-temperature structure of $Al_{60}Ti_{20}Li_{20}$, for a next-nearest interaction of 0.010 meV. Color scheme: Al=grey, Ti=yellow, Li=red. This results in a mixture of AlTi, Al_3Ti, and AlLi phases, for all choices of next-nearest neighbor interactions of the chosen form.

above this temperature. Even a weak interaction of 0.002 eV/bond creates much more order, and a well-defined peak in C_V. As the interaction is made stronger, the heat capacity peak occurs at a higher temperature, and tends toward a higher peak value. Based on these observations, subsequent simulations were performed with next nearest neighbor interactions, primarily with a strength of 0.010 eV/bond.

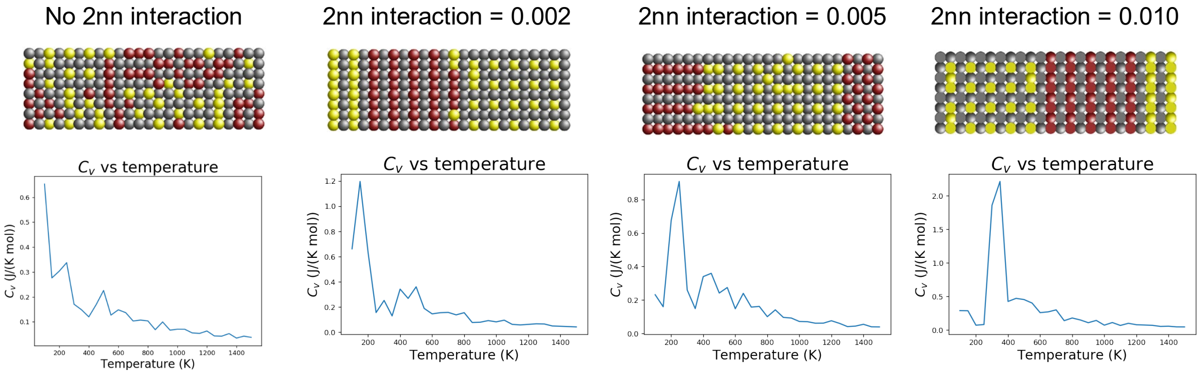

Figure 6. (top) Monte Carlo result for low-temperature structure (~100 K) of $Al_{60}Ti_{20}Li_{20}$, as a function of next-nearest interaction (2nn) strength (in eV/bond). Color scheme: Al=grey, Ti=yellow, Li=red. (bottom) MC simulated heat capacity vs. temperature for each choice of next-nearest-neighbor interaction. A larger value results in a more ordered structure, and a higher transition temperature (as indicated by the peak in the heat capacity C_V).

Similar analyses of phases present and transformation temperature were evaluated for all compositions shown in Figure 1. A particular focus was initially placed on compositions with equal amounts of Al and Ti. These tended to form AlTi plus Li. As Li is a soft, reactive phase, this is not favorable. It may be possible to quench an Al-Li-Ti solid solution: the simulations indicated that a solid solution is present at higher temperatures, but as the system is cooled, the Al and Ti order, and the Li separates out at the same temperature. The calculations showed that this ordering transition occurs at lower temperatures for low Li concentrations. Based on these and other considerations, to avoid forming a pure Li region: one must keep $x_{Al} > x_{Ti}$ (or at least close). For $x_{Al} \leq x_{Ti}$, at low temperatures, all Al goes into Ti, leaving Li.

We also considered more complex alloy compositions, particularly motivated by experimental observations of a single-phase solid solution formed of $Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$ [1]. The reported compound is of interest due to its light weight and reported high strength. Furthermore, the enthalpy matrix (Table 1) indicates that Ti and Sc may interact with other elements similarly, and this is qualitatively known as well from prior studies of Al-Ti and Al-Sc alloys. The simulations show a disordered phase above 650 K, but three ordered phases form at low temperatures: Al_3Sc, Al_3Ti, and LiMg (see Figure 7). Some simulations suggest that this transition occurs in two steps: first, the Al-containing phases order, leaving a Li-Mg solid solution, and at a lower temperature, the Li-Mg phase orders. Indeed, experimentally, Li and Mg form a solid solution for all compositions below 60 at-% Li above 0° C. However, we performed electronic structure calculations which suggest that the five-component solid solution is high in enthalpy, and may be due to the fact that Li tends to form a body-centered cubic (BCC) phase and may have limited solubility. This may also be due to the fact that the calculations ignored short-range order, which we expect to be significant for Al-based compounds with Al-Ti and Al-Sc. Indeed, our simulations indicate that this short range order is significant (see Figure 7).

These observations suggest that a potential alloying strategy for Al-Li-Ti would be to include some Mg. The Mg may form a solid solution at higher temperatures, but segregates with the Li at lower temperatures.

This likely both strengthens the Li-based phase, and certainly increases the melting temperature of the Li-Mg phase (from 181 °C for pure Li, to ~480 °C for $Li_{50}Mg_{50}$).

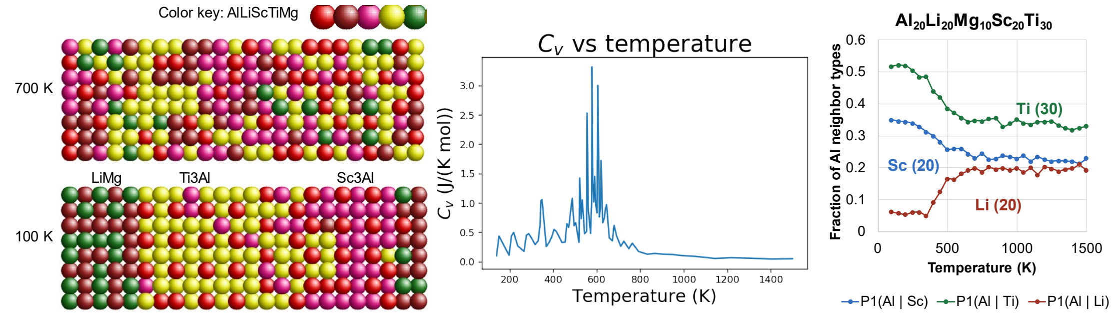

Figure 7. (Left) Monte Carlo results for structures of $Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$ at 700 K and 100 K, choosing the composition from [1]. (Middle) MC simulated heat capacity vs. temperature for this composition. Results show the possibility of forming a single-phase solid solution above ~650 K, qualitatively in agreement with experimental observations [1]. (Right) Al-based short-range chemical order, based upon the MC calculations.

5. SUBJECT INVENTIONS (AS DEFINED IN THE CRADA)

None.

6. COMMERCIALIZATION POSSIBILITIES

This work still remains at the discovery phase. Ultimately, if reasonable lightweight compounds of Al-Li-Ti or Al-Li-Mg-Ti can be found, they could exhibit favorable properties that could be commercialized. We note that the compound in [1], which is both light weight and hard, is likely expensive, due to the large amount of Sc, but our calculations indicate that the Sc may potentially be replaced with Ti.

7. PLANS FOR FUTURE COLLABORATION

We anticipate some on-going collaborations, primarily to complete calculations and publish this work. We see a potential for future collaboration related to this work and related interests, including other work on Al-based systems. However, we do not presently see an avenue to continue this work in a direct collaboration, based on current funding opportunities and current company directions.

8. CONCLUSIONS

This work demonstrates significant steps toward the use of high-throughput calculations and simulations for alloy discovery and design. The choice of Al-Li-Ti compounds was made primarily due to the lack of current thermodynamic information, because of the low melting point of Li, and the high melting point of Ti, as well as the lack of mutual solubility. The work of this project provides some support for pursuing these alloys, and some initial guidance, previously not available, toward compositions that may be useful to explore. The simulations point to the possibility of forming reasonable alloys of Al-Li-Ti, due to the strong attraction of Al with both Li and Ti. This is supported by a recent paper of a 5-component Al-Li-Ti-Sc-Mg single-phase material [1].

This work has identified several points that guide future exploration of these alloys:

- The amount of Al likely must be kept above the amount of Ti (as an atomic fraction), and likely above the amount of Ti plus Li, to avoid the formation of an unfavorable Li phase.

- At 50 at-% Al, the system tends to form TiAl + LiAl. Additional Al likely will result in the formation of Al_3Ti, which may be favorable. The Al_3Li phase is much less likely, due to the favorable Al-Ti attraction, and the marginal stability of the Al_3Li phase relative to Al + AlLi.
- The addition of Mg may be attractive: it favorably forms with Li, and significantly increases the melting point of the Li phase. It may also be useful for strengthening.
- Ti may likely be substituted with Sc (and possibly Zr) in these materials, though this will likely greatly increase cost. We note that Al_3Sc is a known, potentially favorable precipitate for Al, with minimal misfit strain.

ACKNOWLEDGEMENTS

This report reflects the work of the Authors, J. R. Morris and A. Kulovitz, as well as people funded through this project: M. Claudia Troparevsky, Eva Zarkadoula, Markus Eisenbach, Linqing Peng, and Zongrui Pei. JRM would further like to acknowledge discussions with German Samolyuk and Lou Santodonato. Both authors would like to thank the assistance and encouragement of Edgar Lara-Curzio for introductions that made this work possible.

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