

Atomistic Simulation of Dislocations in Mg & Mg-alloys: Interaction between Yttrium Clusters and Dislocations to Improve Ductility of Mg Alloys

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WN 22 Engineering Honors Capstone Project

April 25th, 2022

Abstract

Magnesium is a lightweight structural metal often used in the automobile/aerospace industry. It comes with satisfiable strength, but pure Magnesium exhibits low room temperature ductility, impeding further usage in large-scale productions. Alloying rare earth (RE) elements like Yttrium have been reported to activate more slip systems, leading to a significant increase in ductility compared to pure Mg or other Mg alloys of similar grain sizes. Previous research has revealed the origin of the problem to be its crystal structure and lack of activated slip systems. However, the specific role of RE elements remains unclear, and little research has been done to investigate how the interaction between clusters and dislocations could affect the dislocation glide mechanism. Here Yttrium clusters are points of interest and preliminary results are presented.

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Concepts Explained

Dislocation

Dislocations are 1-dimensional defects (line defects) in materials. A dislocation is a crystallographic defect or irregularity within a crystal structure. The presence of dislocations decides the mechanical, thermal, and irradiation performances of materials, and by studying the underlying mechanism we can manipulate material properties to suit our needs.

There are two common types of dislocations: edge dislocation and screw dislocation. Only screw dislocation will be introduced here because of page limits and the project only make use of screws.

Why do dislocations exist?

From a thermodynamic perspective, dislocations can reduce the total energy of the material by transforming the small-amplitude and spatially diffusive distortion into large-amplitude and spatially localized distortion. To put it in simple words, nature prefers lower energy states, and the existence of dislocations serves that purpose.

From a kinetic perspective, dislocations can facilitate plastic deformation by reducing the energy barrier and the required stress to propagate the plastic deformation.

Screw dislocation

Screw dislocation can be understood by literal meanings, where the structure rotates with respect to a slip plane, leaving some atoms to have higher elevations than others. The origin of dislocations is usually external stresses. Figure 1 shows what a typical screw dislocation looks like.

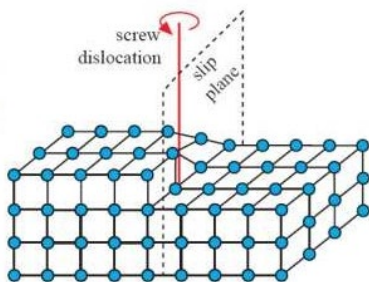


Figure 1. Screw dislocation

Ductility

Ductility is the material property that measures its ability to plastically deform without fracture. In other words, it indicates how soft or malleable the material is when subjected to forces or impacts.

Cluster

From the atomic level, cluster means the atoms are gathered in small groups rather than randomly dispersed (solid solution) or forming large bulks (precipitates). Figure 2 shows an example from this project. The red atoms are Mg while the blue ones are Y. Note that the clusters could segregate to form precipitates.

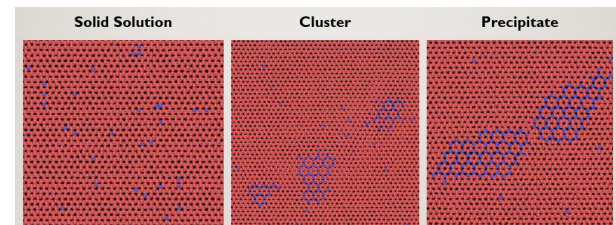


Figure 2. Different materials state at the atomic level (Red – Mg, Blue – Y)

Background

Lightweight structural materials are an essential step towards better energy efficiency and societal well-being. Mg is the lightest structural material that is not only abundant on earth but also recyclable. Its density is about two-thirds of Al and about one-fourth of Fe. It also has satisfactory strength, making it a promising alternative to the traditional Al alloys or steel. However, their low ductility (especially at room temperature) impedes further usage in large-scale productions. For over a decade, intensive experimental and computational studies have focused on this theme and people have found the origin of the issue related to the number of slip systems activated.

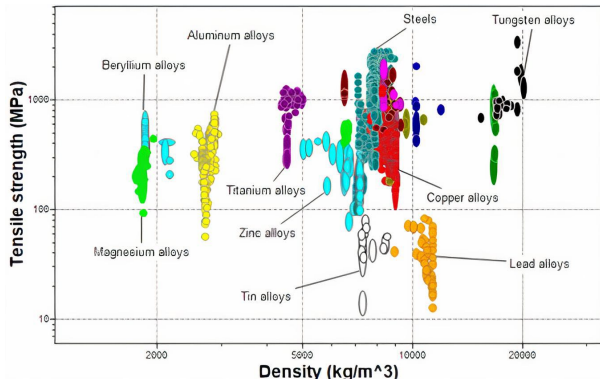


Figure 3. strength vs density plot for common alloys

According to the von Mises criterion, arbitrary plastic deformation requires five independent slip systems to maintain compatibility [1], yet in pure Mg, only activates basal or prismatic slip systems are activated at room temperature, which could only provide two independent slip systems each, and none of them is in the crystallographic $\langle c \rangle$ direction. Therefore, an additional slip system is needed, especially one that could accommodate c -axis plastic strain.

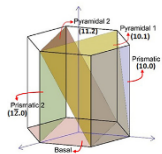


Figure 4. Slip systems in Magnesium crystal

Generalized Stacking Fault Energy (GSFE) and Unstable Stacking Fault Energy (USFE) are important indications of the activation of slip systems. (USFE is the global maximum of GSFE) The GSFE of pyramidal $\langle c+a \rangle$ dislocations is generally twice that of basal $\langle a \rangle$ dislocations [2], leading to the unfavorable activation of $\langle c+a \rangle$ dislocation at room temperature. Another indication is the critical resolved shear stress, where the glide of $\langle c+a \rangle$ dislocations require two orders of magnitude higher force than that of basal $\langle a \rangle$ dislocations [3].

There is no widely recognized mechanism so far, but two strategies have been proposed and accepted by general researchers. The first one involves alloying to tune GSFE and USFE of different slip systems. The second one is associated with alloying to tune $\langle c+a \rangle$ dislocation core structure.

The first strategy stems from the observation that the addition of Y will significantly decrease the USFE of the prismatic slip plane [2]. Compared with pure Mg, the USFE decreased for the three $\langle a \rangle$

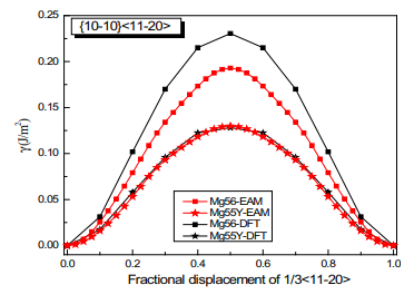


Figure 5. GSFE curves for prismatic slip system [2]

slip systems upon the addition of Y, while the GSFE curve in the pyramidal II system is initially lower but with increasing displacement becomes higher than pure Mg (Figure 3). This finding is confirmed by TEM results.

There is no explicit conclusion as the impact of Y on GSFE is rather complex. For $\langle a \rangle$ dislocations, it reduces both stable and unstable stacking fault energy, but for $\langle c+a \rangle$ dislocations, an increase has been observed at large displacements.

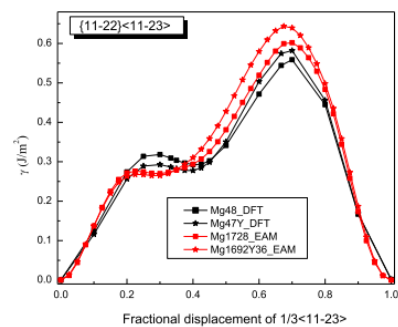


Figure 6. GSFE curves for pyramidal II slip system [2]

The second strategy is based on the observation of a thermally activated, stress-dependent transition of $\langle c+a \rangle$ dislocation to one of the three basal $\langle a \rangle$ dissociated dislocation structures (Figure 4). This transition is believed to be intrinsic to Mg and the resultant structures will act as obstacles to all other easy-glide $\langle a \rangle$ dislocations. [4]

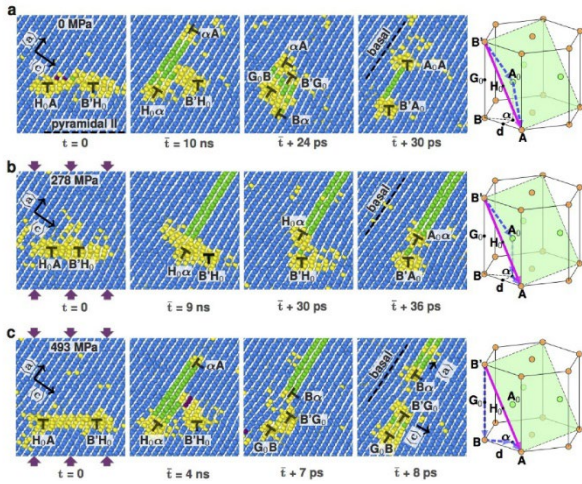


Figure 7. Pyramidal II $\langle c+a \rangle$ dislocation dissociation. Long-time MD result showing the transition of $\langle c+a \rangle$ to three $\langle a \rangle$ dissociated structures with different compressive stresses. Dislocation cores are represented by \perp . Atoms are colored based on common neighbor analysis, blue-hcp, green-fcc, purple-bcc, yellow-others.

If further confirmed by experiments, the implication of this finding is tremendous. Procedures could be aimed at shifting this transition to higher temperatures, longer times, or slower strain rates, which might be possible by the addition of solute atoms/clusters. The atoms/clusters could pin the $\langle c+a \rangle$ dislocation core and subsequently lower its energy.

Based on the two strategies, how the solute atoms interact with dislocation glide is crucial to understanding the problem. There is a potentially new strengthening mechanism hidden behind it. Therefore, Y clusters and their interactions with

dislocations are of interest in this project.

Methods

Constant-temperature Molecular Dynamics

Molecular Dynamics (MD) is a simulation method for computing the equilibrium and transport properties of a classical many-body system. It is based on Newton's equations of motion for a system of interacting particles.

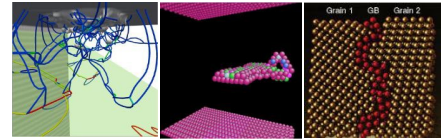


Figure 8. example MD results

Simplified schematic of the molecular dynamics algorithm

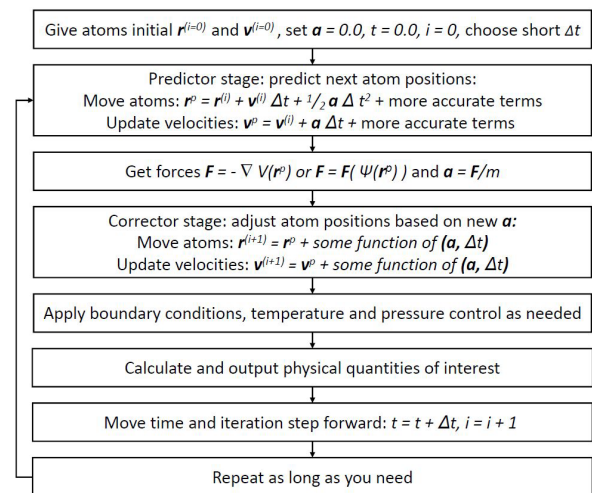


Figure 9. Typical MD schematic [5]

In this project, the MD simulations are utilized to mimic a room temperature environment using various ensembles, including the NPT (constant number of particles, pressure, and temperature), NVT (constant number of particles, volume, and temperature), and semi-grand canonical ensembles. It is also used to find the lowest energy configuration (relaxation).

Monte Carlo – Atom Swap

Monte Carlo usually refers to an algorithm that uses random sampling to obtain numerical results. In this project, Monte Carlo (MC) is embedded in the atom

swapping process. A randomly chosen Mg atom exchanges position with a randomly chosen Y atom and the energy of the new system is calculated. The exchange will happen with probability $\min(1, A)$ where A is proportional to $e^{\frac{-1}{kT}}$. More details can be found in Figure 11.

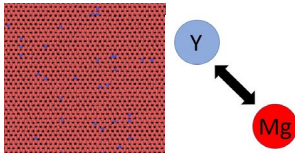


Figure 10. Atom swap illustration

Algorithm 2 (Attempt to Displace a Particle)

<pre> SUBROUTINE mcmove o=int(ranf()*npart)+1 call ener(x(o),eno) xn=x(o)+(ranf()-0.5)*delx call ener(xn,enn) if (ranf().lt.exp(-beta + *(enn-eno)) x(o)=xn return end </pre>	<p>attempts to displace a particle</p> <p>select a particle at random energy old configuration</p> <p>give particle random displacement energy new configuration</p> <p>acceptance rule (3.2.1) accepted: replace x(o) by xn</p>
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Figure 11. Metropolis method schematic [5]

Hybrid MC/MD simulation to observe Y clusters

Hybrid Molecular Dynamics (MD)/ Monte Carlo (MC) simulations are performed in LAMMPS to introduce Y dopants into Mg crystals in order to obtain an equilibrium concentration of Y. During the simulation, MC steps are used to sample the semi-grand canonical ensemble, and MD steps serve the purpose of relaxing the system. Each MC step is followed by 50 MD steps for it to allow sufficient time to find the lowest energy configuration. The probability of swapping Y atoms with Mg atoms is dictated by the Metropolis criterion at 300K. The system is considered to be at equilibrium when the energy fluctuation is less than 0.5% over 10000 steps. The chemical potential difference of 3.10 eV was chosen to achieve the desired 2 at% Y concentration. The timestep is chosen to be 1 femtosecond and 216000 atoms are

contained in the simulation cell. [6]

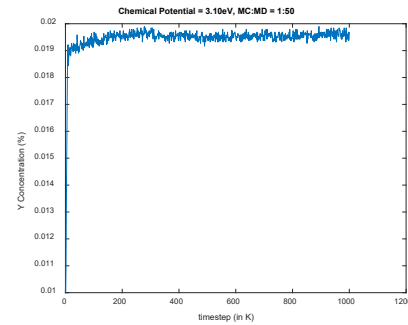


Figure 12. Y concentration evolution with time

Threshold Temperature & Concentration

Threshold temperatures and concentrations are determined based on whether cluster formation happens. For temperature, an increment interval of 25K is investigated from 300K to 1000K. When it reaches 475K, Y clusters no longer form, and the system persists in random Y distribution. Threshold concentrations are determined with an increment interval of 0.01 eV from 2.70 eV to 3.10 eV, and 2.87 eV is the boundary value where no obvious clusters form. The corresponding concentration is around 2.15 at% at equilibrium. However, this remains open to debate as the definition of a cluster is not unique and the boundary is rather vague.

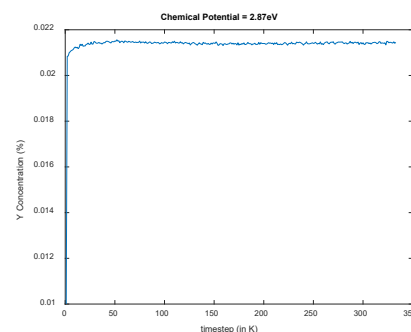


Figure 13. Equilibrium concentration for 2.87eV

Stacking Fault Width of Screw Dislocation

With the goal of introducing dislocations into the system, a single screw dislocation is created in the middle of a cylinder to verify the validity of the

EAM potential. Under the current setup, the Stacking Fault (SF) width equals 3 nm which corresponds to experimental findings of 1-3 nm [7].

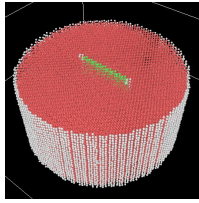


Figure 14. SF Width verification

Colors assigned by common neighbor analysis, green-fcc, pink-hcp, white-other

Cluster Analysis

The cluster analysis in OVITO is a modifier that decomposes particles into clusters based on the cutoff range, which means two particles are considered connected if they are within a specified proximity range, and in this case, the radius of an Mg atom.

Simulation setup

The system used for the defected system with Y has a dimension of 15.5(x)*22.1(y)*4.7(z) nm. The distance between two screw dislocations is 11nm. The temperature is set at 300K, and the MC/MD ratio is 1:50.

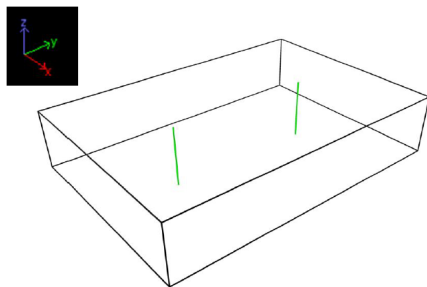


Figure 15. Simulation system setup

Results

Yttrium Cluster in Bulk

Y clusters are successfully identified with the current simulation setup. Starting from a solid

solution state where all Y atoms are randomly dispersed in the system, the formation of clusters can be clearly seen, and as time evolves, the clusters form precipitates.

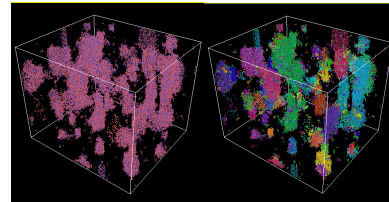


Figure 16. (left) Y atoms with first-nearest-neighbor Mg

(right) Cluster Analysis results in OVITO

Proposed Cluster Structure Match

Based on the number of atoms contained in the clusters identified by Cluster Analysis, a histogram is plotted showing the Y concentration distribution. The large and small clusters are distinguished by the average cluster size (15 atoms), and the 1-atom clusters are not considered clusters thus deleted from this figure.

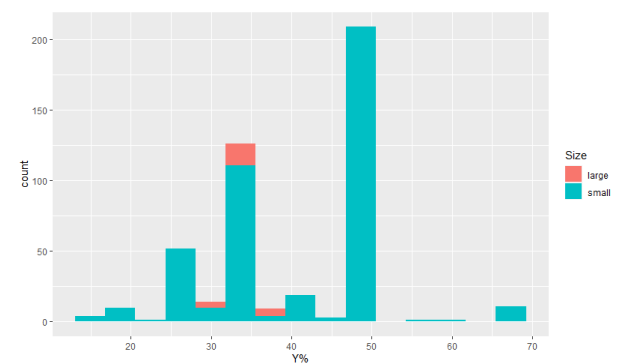


Figure 17. Histogram of cluster Y concentration

As can be seen from Figure 9, large clusters generally have a Y concentration of 30-40%, while for small clusters, it can go from less than 10% to almost 70%.

Based on the MgY phase diagram, only MgY and Mg₂Y are present at 2 at% Y concentration. Four large clusters are zoomed in to see their specific structure and based on the pairwise distances as

well as their tetrahedral motif, it is reasonable to guess that the large clusters could be Mg_2Y . The pairwise distance between two atoms is also compared to the perfect Mg_2Y structure to confirm.

Evidence of cluster-dislocation interaction

When the system energy converges, Y atoms are found to cluster around dislocation lines as shown in Figure 18 and Figure 19 (true for both EAM and MEAM potential). We can see that the Y concentration around the two dislocation lines is significantly higher than in any other location. Note that the maximum does not overlap exactly where the dislocation line is, which could be due to the reason that these line plots are based on a single simulation snapshot and therefore could have some numerical noise. A next step could be to use the averaged value based on the last 1000 steps to get a more accurate result.

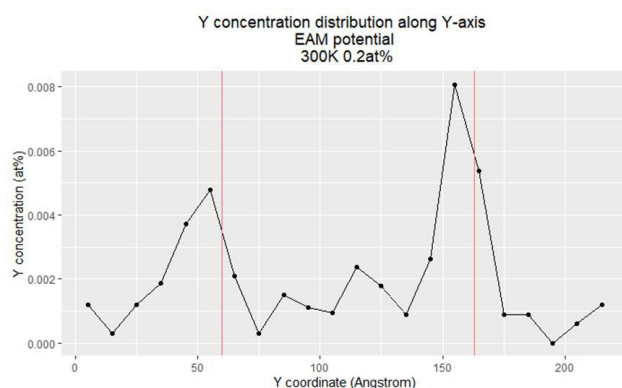
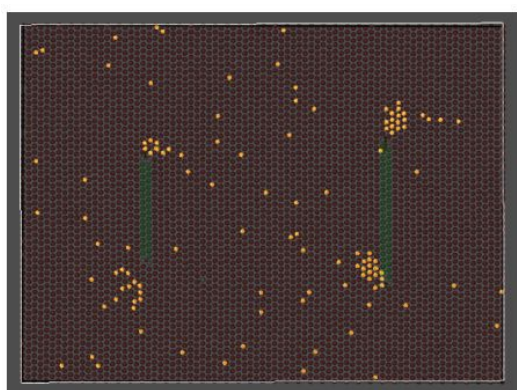


Figure 18. Y cluster-dislocation interaction using EAM potential (Yellow – Y, Red – hcp, green – fcc, white – other)

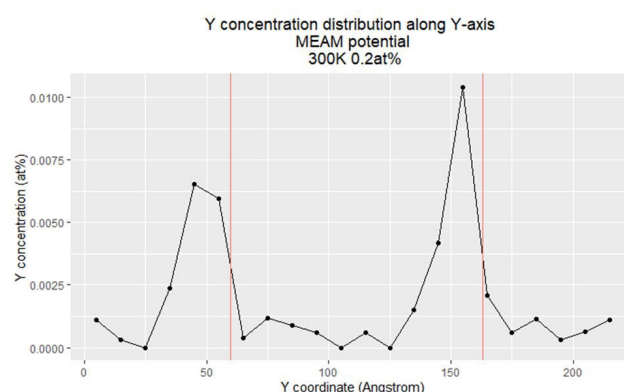
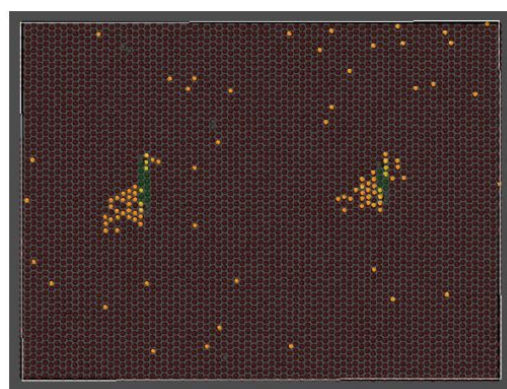


Figure 19. Y cluster-dislocation interaction using MEAM potential

Critical Y concentration (to form clusters)

The critical Y concentration that forms clusters is found for the potentials used as summarized in the table below.

Type	Y_{cr} (at%)
Bulk EAM	0.3
Bulk MEAM	0.2
Defect EAM	0.1
Defect MEAM	0.1

Table 1. Critical Y concentration table

Discussion

The successful observation of Y clusters remains questionable. The shape observed in the simulation does not align with experiments where the same amount of Y dopants are introduced. In the simulation, the shape appears to be ellipsoid and thin plates, while spherical-shaped clusters are observed in experiments. Lack of information

makes it hard to explain the difference.

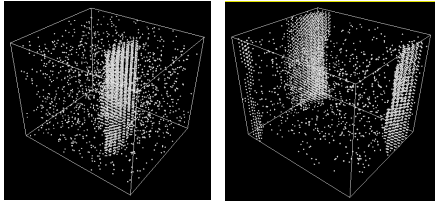


Figure 20. Plate-shaped Y clusters

The proposed match between large clusters and Mg_2Y needs further confirmation and more indications. Despite similarities between pairwise distances and Y concentration, Mg_2Y is not stable at room temperature and will eventually decompose into MgY and Mg_3Y . The structure of large clusters is rather complex and only part of it is tetrahedral-shaped, with the majority cannot be easily categorized into known geometries.

The SF width is best confirmed if consistent among various methods including analytical calculations in anisotropy, MD, DFT, and experiments. The analytical solution is available on *Theory of Dislocation* by John Hirth. I have done the analytical calculations but got 1.8 nm SF width which is inconsistent with my MD results. I'm currently working on resolving the issue.

Future work to confirm the cluster-dislocation interactions includes finding appropriate solute segregation and interaction models as well as applying different external conditions (shear stress & temperatures).

The ultimate goal would be to find replacements for RE solutes to lower costs before we can finally make Mg alloys cheap and ductile, and some research had already identified candidates in this direction. For example, ternary and quaternary alloys of Zn, Al, Li, Ca, Mn, Sn, K, Zr and Sr at dilute concentrations have shown a good ductility.[8]

A brief long-term goal is provided in Figure 21.

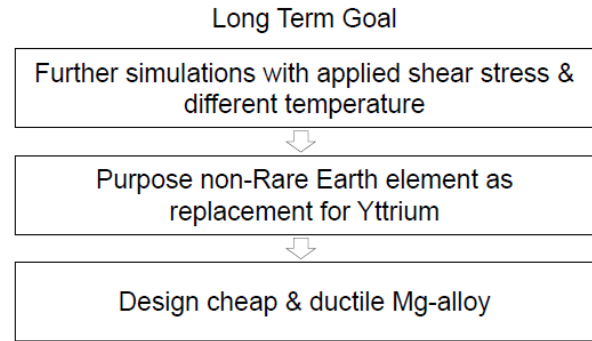


Figure 21. Long-term plan

Acknowledgment

I would like to thank Dr. Liang Qi for providing guidance and resources that made this project possible. I would also like to thank Mr. Tony Wang who provided financial support during the summer, and Vaidehi Menon who provided suggestions on LAMMPS script writing.

References

- [1] J.P. Hirth, J. Lothe, Theory of Dislocations, 2ed., John Wiley & Sons, 1982
- [2] Pei, Z., et al. "Ab initio and Atomistic Study of Generalized Stacking Fault Energies in Mg and Mg–Y Alloys." *New Journal of Physics*, vol. 15, no. 4, 2013, p. 043020. Crossref, doi:10.1088/1367-2630/15/4/043020.
- [3] Yin, Binglun, et al. "First-Principles Calculations of Stacking Fault Energies in Mg-Y, Mg-Al and Mg-Zn Alloys and Implications for $\langle c+a \rangle$ Activity." *Acta Materialia*, vol. 136, 2017, pp.249–61. Crossref, doi:10.1016/j.actamat.2017.06.062.
- [4] Wu, Zhaoxuan, and W. A. Curtin. "The Origins of High Hardening and Low Ductility in Magnesium." *Nature*, vol. 526, no. 7571, 2015, pp. 62–67. Crossref, doi:10.1038/nature15364.
- [5] Frenkel, Dann, and Berend Smit. *Understanding Molecular Simulation - From Algorithms to Applications (2nd, 02) by [Hardcover (2001)]*. Academic, Hardcover(2001), 2022.
- [6] Kazemi, Amirreza, and Shengfeng Yang. "Effects of Magnesium Dopants on Grain Boundary Migration in Aluminum-Magnesium Alloys." *Computational Materials Science*, vol. 188, 2021, p. 110130. Crossref, doi:10.1016/j.commatsci.2020.110130.
- [7] Yasi, J. A., et al. "Basal and Prism Dislocation Cores in Magnesium: Comparison of First-Principles and Embedded-Atom-Potential Methods Predictions." *Modelling and Simulation in Materials Science and Engineering*, vol. 17, no. 5, 2009, p. 055012. Crossref, doi:10.1088/0965-0393/17/5/055012.
- [8] Curtin W.A., Ahmad R., Yin B., Wu Z. (2020) Design of Ductile Rare-Earth-Free Magnesium Alloys. In: Jordon J., Miller V., Joshi V., Neelameggham N. (eds) *Magnesium Technology 2020*. The Minerals, Metals & Materials Series.

Springer, Cham. https://doi.org/10.1007/978-3-030-36647-6_5