Filling in the Blanks for the Unit Cell of Hafnium-Doped Nitinol

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Bachelor of Science

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ABSTRACT

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Nickel Titanium, or nitinol, is a widely used shape memory alloy with many desirable properties and applications. It has been found that when hafnium is added in small proportions the resulting alloy has increased hardness in addition to the shape memory properties of nitinol. Imaging technology has shown that HfNiTi is made of two repeating structures: one that is similar to what is found in NiTi, and another which is suspected to be the source of the increased hardness. As a result, there is great interest in further analyzing the structure of this second phase. To accomplish this, an interatomic potential obtained through machine learning was used to construct a genetic algorithm. Because low formation enthalpy is an indicator of stability, this algorithm used the interatomic potential to optimize the formation enthalpy for an alloy of HfNiTi with atomic percentages of about 9%, 60%, and 31% respectively. By running this genetic algorithm on progressively larger unit cells, we found new metastable states of HfNiTi.

Keywords: HfNiTi, Nitinol, Interatomic potential, MTP, γ-brass,

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Chapter 1

Introduction

Nickel titanium, also called nitinol or NiTi, is a shape memory alloy with many useful properties. A shape memory alloy is a metallic alloy that can be restored to its remembered state after deformation when it is heated up. In particular, nitinol's remembered state can be set by shaping it and letting it rest for several minutes at temperatures around 500°Celsius. Shape memory alloys have a wide array of uses ranging from industry to medical. For example, medical implants can be inserted into the body while deformed, and then returned to their original shape.

1.1 HfNiTi

Because shape memory alloys are so useful, there is great interest in analyzing them further and finding ways to improve their properties [1, 2]. One way to enhance nickel titanium, for instance, is to add another element to it.

One good option for the third element is hafnium, because both titanium and hafnium are in the same family, so they are likely to act chemically similar. Hafnium will interact in a similar way to nickel as titanium does, but the higher atomic mass will be beneficial for the alloy.

So far, numerous experiments have found that small amounts of Hf improve the properties of the

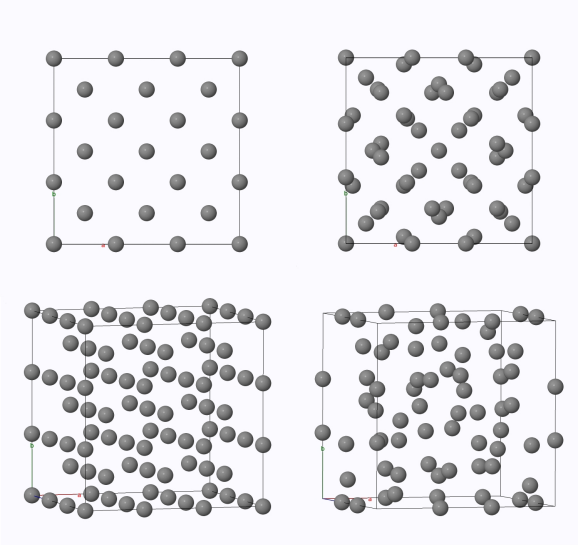

Figure 1.1 The two possibilities for the unit cell of HfNiTi: 3x3x3 BCC (left) and $\gamma-$brass (right), which contain 52 and 54 atoms respectively. The spheres represent locations where the atoms can be. They are all gray because while the positions are known, the type of atom that goes in each location is unknown [3].

alloy. In particular, one paper authored by Aaron Stebner and others [2] details some of the benefits, including increased hardness and ability to withstand higher stress. The optimal atomic percentages they found were 8% Hf, 56% Ni, and 36% Ti. The hafnium-nickel-titanium alloy (HfNiTi) that Stebner researched was the main topic of my research

1.2 Atomic Configurations

When Aaron Stebner looked at the atomic structure of HfNiTi, he found that there are two main crystal structures in the alloy: one that is very similar to the crystal pattern of nitinol, and another that is more complicated. The second crystal is made up of a repeated pattern, or unit cell, of either 52 or 54 atoms, as shown in Fig. 1.1. This second crystal is likely where most of the observed improvements over standard nitinol come from.

Because of the limits of imaging technology, Aaron Stebner was only able to determine the

shape of the unit cell. The positions where atoms are located were known, but the type of atom located at each position was unknown. The main goal of my research was to use the data provided by Aaron Stebner to construct the unit cell for the crystal he observed in his HfNiTi alloy.

Chapter 2

Methods

To find the configuration for the HfNiTi crystal, we needed to fill in the blanks for the suspected unit cell shapes (Fig. 1.1). We did this by systematically exploring randomized configurations that matched these shapes and using and ruling out the least stable ones.

2.1 Convex Hull

To measure the stability of the configurations, I used a construction called a convex hull [4]. The convex hull is a mathematical model that determines which configurations of atoms are stable by comparing their energies. Specifically, the formation enthalpy and the stoichiometry, or amount of each atom in the configuration, are used to construct the hull.

Formation enthalpy, H is calculated by taking the difference between the energy of a configuration of atoms and the energy that its individual components would have if they were in their single element crystals. For example, a configuration with 5 Hf, 28 Ni, and 21 Ti might have an energy of -429 eV. The average energies of pure Hf, Ni, and Ti are -9.95, -5.58, and -7.34 eV per atom respectively. We calculate the formation enthalpy as

$$H_f = -429 - [5(-9.95\ \text{eV/atom}) + 28(-5.58\ \text{eV/atom}) + 21(-7.43\ \text{eV/atom})] = -66.98\ \text{eV}$$

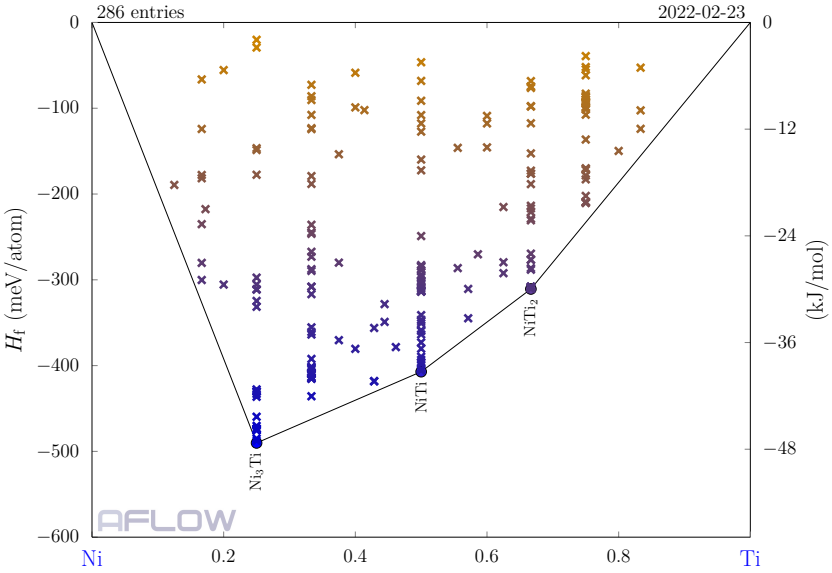

Figure 2.1 The binary convex hull for nickel and titanium [3]. The x-axis shows the fraction of atoms in the configuration which are titanium. The convex hull can be visualized as a rubber band stretched around a series of pegs. The pegs that are touched by the rubber band are stable configurations, while the ones inside are unstable.

In general,

$$H_f = E_{\text{tot}} - \sum_i n_i \cdot e_i \tag{2.1}$$

where n_i and e_i are the number and average energy per atom for the atom i respectively.

Convex hulls are more easily explained for binary alloys. Consider Fig. 2.1: each data point represents a theoretical configuration of atoms for which the formation enthalpy has been computed. The stable configurations, the ones that can actually occur, are connected by the line. The line itself is the convex hull in two dimensions. If researchers found a configuration containing 90% Ni and 10% Ti, with formation enthalpy that fell bellow the value of the line at that point, about -0.18

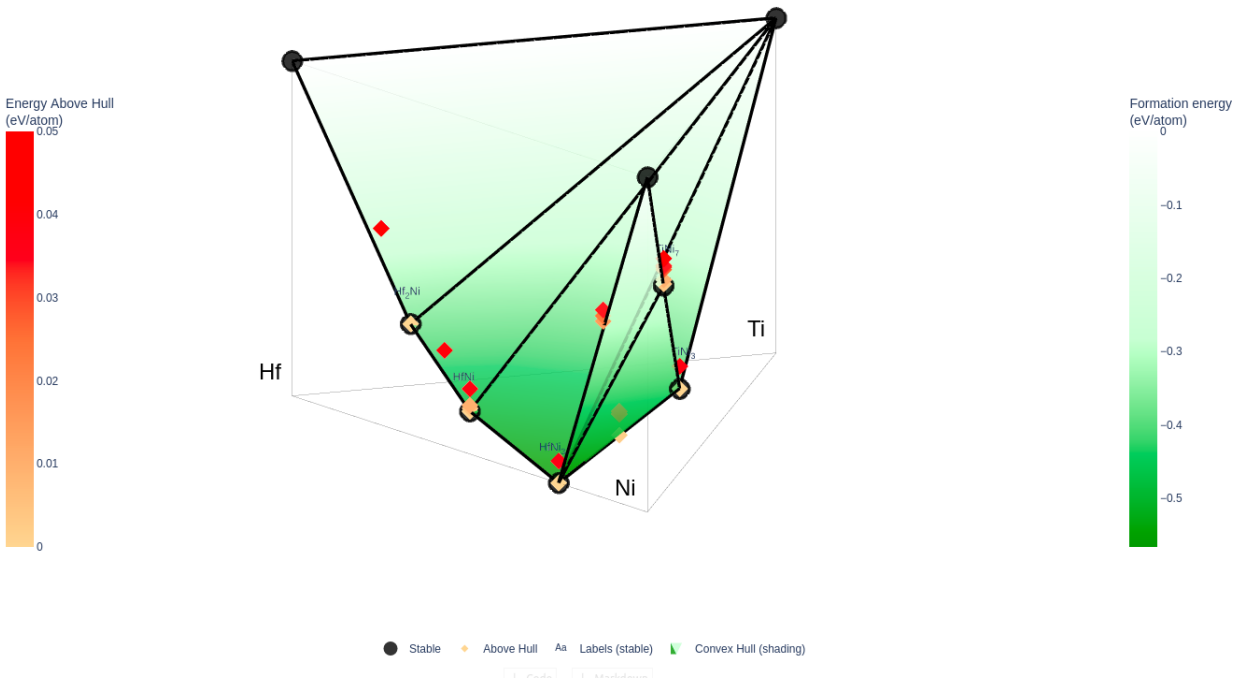

Figure 2.2 The ternary convex hull for hafnium, nickel, and titanium (HfNiTi); it contains all known stable configurations involving these three elements, and shows some other unstable configurations that I have tested. There are no stable data points representing crystals which contain all three elements, but we know that a stable configuration of HfNiTi exists.

eV/atom, then they would construct a new convex hull with six points and five lines connecting them. A ternary convex hull is similar in concept, except in three dimensions. In this case, rather than being a series of lines, the convex hull is a series of plane segments. To determine whether a configuration with a certain stoichiometry is stable, it must have a formation enthalpy less than the value of the convex hull with the same stoichiometry. This is what I mean whenever I reference a configuration "bellow the convex hull".

2.2 Potential Modeling

There are far too many possible 52- and 54-atom unit cells (on the order of 10^{25}) to calculate the formation enthalpy of each and compare them to find the optimal configuration, so we needed to find ways to speed up the process. First, finding the exact atomic interactions is a long and difficult process, especially for configurations of this size. Second, we had to be able to find the configuration with the lowest formation enthalpy without systematically testing every single possible configuration. To solve these problems, we used machine learning and a genetic algorithm.

To find the unit cell of HfNiTi, a method of finding the interactions between particles without running extensive and computationally expensive interatomic modeling programs was necessary. A machine learning algorithm called Machine Learning Interatomic Potentials (MLIP), developed by Alexander Shapeev at Skoltech, Russia, was employed. His program uses data points made of configurations of specific kinds of atoms and the associated energies and forces between them to make a model called a moment tensor potential (MTP) [5]. The MTP can then be used to approximate the forces between any configuration using those specific atoms. My advisor and I used thousands of configurations involving combinations of hafnium, nickel, and titanium to train an MTP that would accurately and quickly find the potential energy of a group of these atoms.

When we obtained this model, the next step was to pick which configurations of atoms to

calculate the potential energy for. Without any data on the energy of such large unit cells, randomly generated configurations were the best option. We did this by creating random arrays containing the numbers '0', '1', and '2', representing 'Hf', 'Ni', and 'Ti' respectively. Then a program would create an atomic configuration by assigning each element to a position according to its index in the array. We then used our MTP to find the potential energy of the configurations. By running this process on 1000 random configurations, we obtained enough data to begin implementing a genetic algorithm to help find configurations that are more likely to be stable.

2.3 Genetic Algorithm

Genetic algorithms are extremely useful tools: by allowing us to explore countless possibilities through only using a small fraction of the total combinations, we can optimize a parameter of interest. In this case, it would allow us to find the spot on the convex hull corresponding to the known approximate atomic percentages by sampling thousands of configurations rather than 10^{25}. These algorithms work by taking many samples and measuring their properties. Then the more optimal samples are combined to generate a new generation of samples, and the process is repeated until the samples converge on the optimal configuration.

An important part of a genetic algorithm process is determining which samples to select as parents, and how to combine them to create children. The method I employed was tournament style selection: I randomly shuffled the samples and divided them into groups of N contestants. The one in its group which was closest to the convex hull was chosen for a parent, and the parents were randomly combined to create a new configuration. I would repeat this process N times so that the number of new samples was equal to the number of old samples.

Distance to the convex hull is a more complicated parameter than just energy. First we had to calculate the formation enthalpy. That is done by taking the difference between the energy of the

configuration and the average energy of the stable configuration for each atom multiplied by that type of atom.

A problem I ran into was that after many iterations of this algorithm was getting stuck in local minima, some of the samples tended to be repeated, and eventually came to make up the majority of my samples. As they didn't rest on the convex hull, they weren't what I was looking for. One way to get past this is by introducing a lockstep protocol [6]. This involves classifying certain configurations as forbidden to reduce these repetitions. Since some repetition is a sign of a favorable sample, I set the bar such that if over 25% of the samples were the same, that particular configuration would be added to the forbidden list. If a newly generated sample matched one of the configurations on the forbidden list, I would try to combine the two parents in a different way, and if that didn't work, I would use the parents themselves. If both those steps failed, I generated a new random structure. In this way, my genetic algorithm was able to overcome the local minima to find the true optimal configuration.

Chapter 3

Results

Because there are such a large number of possible configurations for the 52- and 54-atom unit cells, it would take my genetic algorithm far too long to find anything with low energy by running it directly on cells of that size. To get past this problem, I ran my algorithm on smaller configurations and used the results to build up to larger configurations by including the smaller configurations within the larger ones among the first batch of configurations to be run through the genetic algorithm.

I started with a 6-atom unit cell, because 6 divides 54 and is small enough to run many iterations in the genetic algorithm in a short amount of time. The 6-atom configuration reached formation enthalpies of about 12 meV/atom, which wasn't enough to be close to the convex hull, but was a step in the right direction. For reference, when I generated 1000 random 54-atom configurations, most of them were over 100 meV/atom above the convex hull, and one or two would be about 50 meV/atom above.

Another configuration size I tested was 12-atoms. My genetic algorithm found many 12-atom configurations with formation enthalpies much closer to the convex hull than the 6-atom configurations. The low-energy 12-atom unit cells are interesting because they contain a wide variety of stoichiometries. For example, one contains two hafnium, five nickel, and five titanium while another has seven hafnium, four nickel, and one titanium. My advisor and I suspect that the

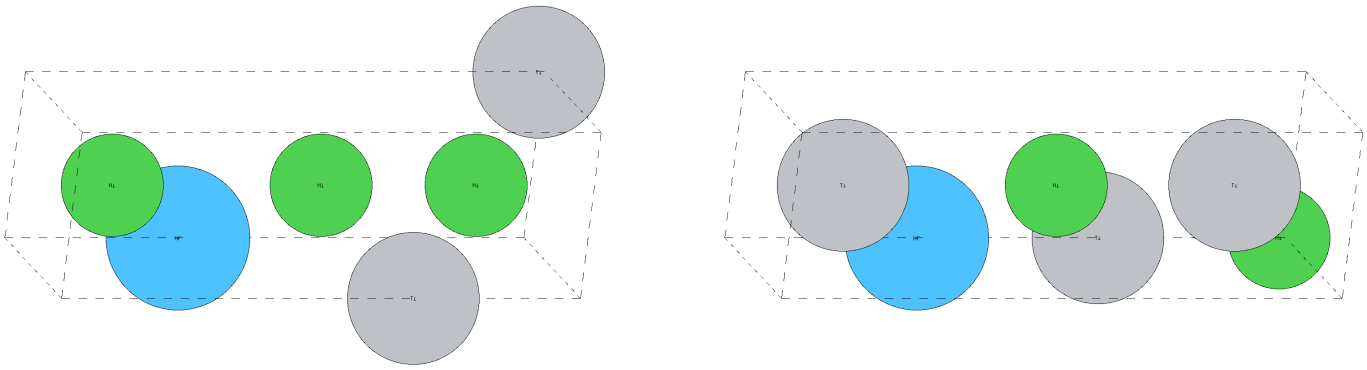

Figure 3.1 These are two of the lowest-energy 6-atom configurations I found. Blue represents hafnium, while green and gray represent nickel and titanium respectively. The one on the left was about 17.6 meV/atom above the convex hull, and the one on the right was about 17.3 meV/atom above the convex hull [7].

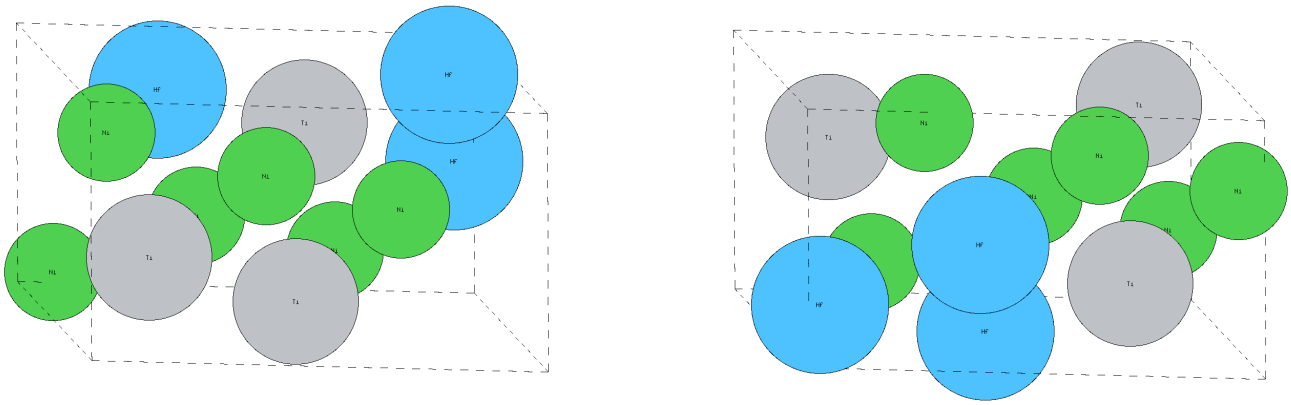

Figure 3.2 The 12-atom configurations were the first to reach formation enthalpies of less than 10 meV/atom above the convex hull. The formation enthalpies above the convex hull for these cases are both close to 1.95 meV/atom [7].

large 52- or 54-atom unit cell that we are looking for contains one or more structures that looks similar to the 12 atom unit cells we tested.

With data from the 6- and 12- atom configurations, we constructed and tested configurations with 18 atoms. There were far fewer low-energy configurations with 18 atoms than with 12, but

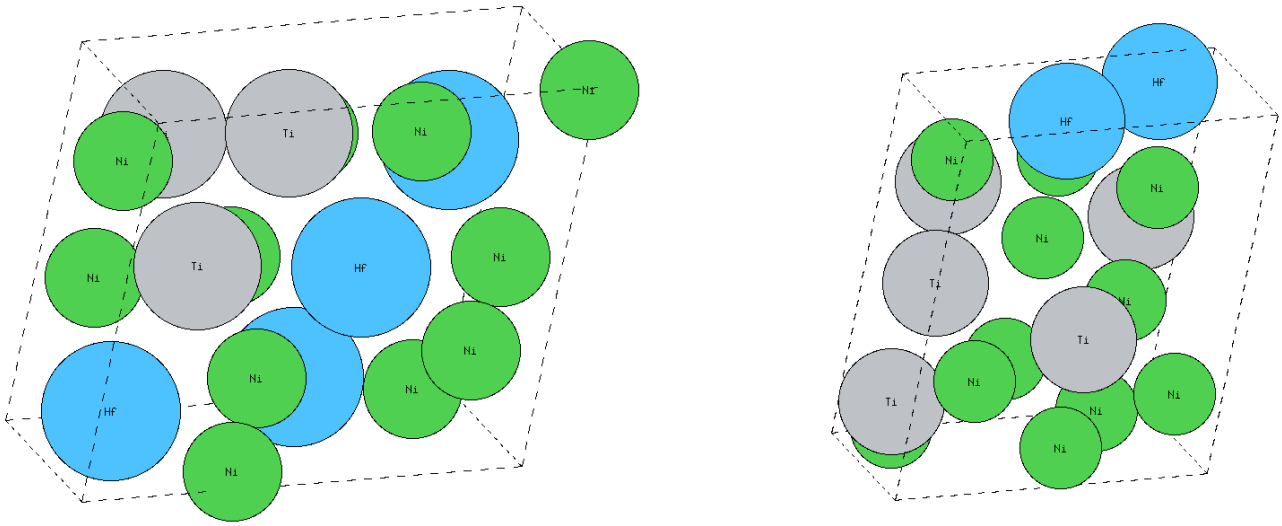

Figure 3.3 The 18-atom configurations got slightly closer to the convex hull than the 12-atom ones. The formation enthalpies above the convex hull for these cases are 1.88 meV/atom (left) and 0.55 meV/atom (right) [7].

the larger configurations still. Unfortunately, although 18 divides 54, the low energy 18 atom configurations had the wrong shapes for them to be transferred to the 3x3x3 BCC supercell shape.

3.1 Conclusion

While the basis of the full unit cell is still unknown, we have found evidence that there is a stable configuration of these atoms and we now have some smaller configurations which could be combined in order to bring us closer to the full unit cell.

In the future, the results that I have obtained can be used to find the most likely candidates for the full unit cell, allowing future researchers to further analyse the properties of HfNiTi. Additionally, the process that I used, including constructing an interatomic potential model and running a genetic algorithm, may be used to find other stable configurations for alloys of interest.

Appendix A

Genetic Algorithm

To begin with, I randomly generated 1000 vectors filled with 0's, 1's, and 2's, representing hafnium, nickel, and titanium respectively, with lengths corresponding to the number of atoms in the unit cell that they were representing. Then I ran them through a program that assigned each atom a position in the unit cell according to its index in the vector. After that, I used the MTP to find each unit cell's potential energy, and compared each one to the convex hull.

Since each vector now had a distance above the convex hull associated with it, I could select parents for the new generation based off that distance. I used a tournament selection to get the parents: I randomly shuffled my list of vectors, and then compared them to each other in groups of n. For example, if n was 5, I would take the first five vectors in my shuffled list and choose the one with the lowest distance above the convex hull to be the first parent. The next parent would be taken from the next five vectors.

I used this pair of parents to make two children by splitting each vector at the same random index and combining the first part of the first parent with the last part of the second parent to make the first child, and vice versa for the second child. Going through the entire list of vectors like this produces 1/5 of the total vectors needed, so I would reshuffle the list and go through the whole process four more times. Then I would begin the next iteration with the new list of vectors.

Appendix B

VASP

VASP is a program that solves quantum mechanics equations to find the potential energy of a configuration of atoms as well as other properties. VASP was used to find the potentials we used for the data we used to build the HfNiTi MTP. We also used VASP to verify some of our results from the 52- and 54-atom unit cells whose potential was obtained from the MTP. To use vasp on the supercomputer, you need to contact Gus Hart to be added to the fsl group fsl_msg_vasp. This will give you access to the vasp_std executable, as well as a multitude of POTCARs.

Appendix C

MLIP and MLIPPY

To use MLIP on the supercomputer, you only need to load some modules to have access to all of the commands:

```
module load intel-compilers/2017 libfabric/1.8 intel-mpi/2017 mlp/0.2
```

Note that one or more of these modules prevents vasp from running properly.

To build mlip on your own device, you must fill out the form at https://mlip.skoltech.ru/register/ to get access to the gitlab repository.

MLIPPY is an extension of MLIP that allows you to use the package from python. To use it, you must get access to the mlip GitLab page. From there you can switch to the mlippy branch and follow the instructions to build the package. It might be helpful to add these folders to the python path prior to compiling:

```
export LD_LIBRARY_PATH=$LD_LIBRARY_PATH:/apps/intel_parallel_studio_xe
/2017_update8/compilers_and_libraries_2017.8.262/linux/mpi/intel64/lib:
/apps/libfabric/1.8.0/lib:/apps/intel_parallel_studio_xe/2017_update8
/compilers_and_libraries_2017.8.262/linux/compiler/lib/intel64:/apps
/intel_parallel_studio_xe/2017_update8/compilers_and_libraries_2017.8.262
```

/linux/mkl/lib/intel64/

Appendix D

Pymatgen

To construct the convex hull of all my samples, I used the pymatgen python package, specifically, I imported pymatgen.analysis.phase_diagram. I found that the most recent version of pymatgen at the time of my writing doesn't work properly in the python environment I created. If you find this to be the case, then using an older version should fix the problem:

```
python -m pip install pymatgen==v2021.3.3 --force-reinstall
```

These were some of the most useful pymatgen.analysis.phase_diagram (PD) commands I found:

```
atomic_configuration=PD.PDEntry([symbols],[energy])
chull=PD.PhaseDiagram([list atomic configurations])
chull.get_e_above_hull([atomic configuration])
```

These put the atomic configurations into data structures that pymatgen can read, create a phase diagram object from the converted atomic configurations, and show the energy above the convex hull for a configuration respectively.

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Glossary

alloy A combination of two or more atomic metals. When the material is solid, the atoms are organized into stable crystals. For a ternary alloy like HfNiTi, there may be one to three different crystal bases in the alloy depending on the atomic proportions. 1

convex hull A mathematical model that marks stable crystal bases using formation enthalpy. The points on the hull represent configurations which have low enough formation enthalpy to occur. 4

crystal A repeating pattern of atoms. The pattern which gets repeated is called a basis. 4

MTP Moment tensor potential; a mathematical model created through machine learning which approximates the potential energy between atoms. 7

shape memory alloy A shape memory alloy is a material that can be restored to its previous shape when heated up after it has been deformed. 1

Bibliography

[1] P. Clayton, "Tribological behavior of a titanium-nickel alloy," Wear **162-164,** 202–210 (1993), wear of Materials: Proceedings of the 9th International Conference.

[2] S. H. Mills, C. Dellacorte, R. D. Noebe, M. J. Mills, A. P. Stebner, and B. Amin-Ahmadi, "Heat treatment – microstructure – hardness relationships of new nickel-rich nickel-titanium-hafnium alloys developed for tribological applications," Materialia **16,** 101064 (2021).

[3] D. U. Center for Autonomous Materials Design, Materials Science, "Automatic flow for materials discovery,".

[4] A. L. Voskov and G. F. Voronin, "A universal method for calculating isobaric-isothermal sections of ternary system phase diagrams," Russian Journal of Physical Chemistry A **84,** 525–533 (2010).

[5] I. S. Novikov, K. Gubaev, E. V. Podryabinkin, and A. V. Shapeev, "The MLIP package: moment tensor potentials with MPI and active learning," Machine Learning: Science and Technology **2,** 025002 (2021).

[6] V. Blum, G. L. W. Hart, M. J. Walorski, and A. Zunger, "Using genetic algorithms to map first-principles results to model Hamiltonians: Application to the generalized Ising model for alloys," Physical Review B 72 (2005).

[7] A. H. Larsen *et al.*, "The atomic simulation environment—a Python library for working with atoms," Journal of Physics: Condensed Matter **29,** 273002 (2017).

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