**New Zirconium Hydrogen Second Nearest
Neighbor Modified Embedded Atom Method
(MEAM) Potential For Simulation of Stacking
Fault Energy Along the $\langle 01\bar{1}0 \rangle$ Path Of The
Hexagonal Closely Packed Lattice Basal Plane**

by

Nenad Vuksic, B.Sc.

A thesis submitted to the
Faculty of Graduate and Postdoctoral Affairs
in partial fulfillment of the requirements for the degree of

Master of Applied Science in Aerospace Engineering

Ottawa-Carleton Institute for Mechanical and Aerospace Engineering
Department of Mechanical and Aerospace Engineering
Carleton University
Ottawa, Ontario
January, 2014

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Abstract

A new Modified Embedded Atom Method (MEAM) potential for zirconium and hydrogen, called the second nearest-neighbor MEAM (2nnMEAM), was created to more effectively simulate the stacking fault energy of different zirconium hydrogen solid solutions along the $\langle 01\bar{1}0 \rangle$ path of the hexagonal closely packed (hcp) lattice basal plane. The 2nnMEAM is a binary alloy MEAM with a less severe screening function that enables the potential to include longer range interactions between atoms. The 2nnMEAM is required because the existing MEAM potential for zirconium and hydrogen, developed by Dr.M.Baskes (in the text referred to as the MEAM potential), although useful for bulk tests of basic physical properties of different zirconium hydrogen phases, was not capable to model the energetics associated with basal slip.

Several previous papers outlined the process of creating binary alloy MEAM potential out of the MEAM potentials of different pure elements. Due to the fact that there is no direct method of combining pure elements MEAM data, a trial and error approach was used to gradually achieve qualitative similarity with the first principles results. This translated into physical behavior, the goal was to show that the 2nnMEAM can be fine-tuned to replicate realistic response of the material during the tests and demonstrate the power of the MEAM methodology. The quantitative agreement was not achieved due to too many unknown MEAM parameters, lack of their physical meaning and functional influence on each other. Furthermore, none of the academic papers used as the basis for this research ventured into more complex tests like stacking fault, but bulk ones, and even then stressed the approximate nature of the MEAM methodology compared to much more precise first principles simulations.

As a main tool for simulating behavior of different zirconium hydrogen solid solutions and testing of different MEAM versions, Large Scale Atomic/Molecular Massively

Parallel Simulator (LAMMPS) [7] program was used. The new 2nnMEAM is shown to achieve qualitatively better agreement with the first principles results for basal slip, while still correctly predicting bulk properties.

Motivation for this research is to contribute to the problem of the Delayed Hydride Cracking (DHC) by means of empirical potentials and atomistic simulations. The new 2nnMEAM would be a starting point for more advanced analysis of MEAM creation methodology and a better simulation of the cracking of the zirconium-hydride interface.

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Nomenclature

2nnMEAM	Second nearest-neighbor MEAM
a, c	Lattice constants
BCC	Body centered cubic lattice
B	Bulk modulus
C	Screening parameter
CANDU	CANadian Duterium Uranium nuclear reactor
C_{ij}	Elastic constants
EAM	Embedded Atom Method
C_{min}, C_{max}	Min. and max value of the screening parameter C
DFT	Density functional theory
DHC	Delayed Hydride Cracking
E_{coh}	Cohesive energy
$E^u(R)$	Energy per atom in a reference structure
$E_{ex}(f)$	Excess energy
$\vec{f}$	Slip displacement vector
FCC	Face centered cubic lattice
γ	Generalized stacking fault energy
Γ	Angular dependency factor
γ_{US}	Unstable stacking fault

$G(\Gamma)$	Angular dependency function
HCP	Hexagonally close packed lattice
LAMMPS	Large Scale Atomic/Molecular Massively Parallel Simulator
LWR	Light water nuclear reactors
MEAM	Modified Embedded Atom Method potential
$\phi(R)$	Pair potential
$\bar{\rho}$	Background electron density
S_{ikj}	Screening factors
S_{ij}	Screening function
θ	Ratio of the number of H and Zr atoms
UBER	The Universal Binding Energy Relation
Z_1	The number of the first nearest-neighbor atoms
Z_2	The number of the second-nearest neighbor atoms

Chapter 1

Introduction

Delayed hydride cracking (DHC) is an important phenomena, particularly in the nuclear industry, requiring a detailed understanding of interactions between zirconium and hydrogen atoms, formation/dissolving of different hydrides and interfaces between hydrides and the bulk of the material. The process itself drastically changes properties of zirconium alloys used in fuel channels in heavy water nuclear reactors. Hydride platelets formed during DHC align themselves with the crack tip on the surface of the fuel channel. After each aligned platelet cracks, another one is generated. The process continues and the crack penetrates deeper into material. This is a complex problem and solving it requires progress and understanding both in experimental and theoretical fields of DHC, as well as more atomistic and DFT simulations about hydrogen in zirconium.

Our scope is to approach this problem from the atomistic level and utilize atomistic simulations to determine the behavior of zirconium-hydrogen solid solutions during slip. In order to do that, we need to create a new empirical 2nnMEAM potential for the zirconium-hydrogen system, and test its ability to precisely simulate the excess energy during stacking fault tests [4]. Those tests were used to determine the origin of the hydrogen embrittlement of zirconium alloys and fracture properties of zirconium hydrogen solid solutions and hydrides. As such, they can be related to the DHC problem and are suitable for fine-tuning of the new 2nnMEAM potential that might be used in the future in direct DHC experiments of fracture of zirconium hydride and $\alpha\text{Zr}/\beta\text{Zr}$ interface.

An important parameter for determining brittle-to-ductile transition and dislocation mobility in the material is the unstable stacking fault γ_{US} . It is the peak excess energy during stacking fault tests. By calculating the excess energy change during

ideal slip between slabs, with different concentration of hydrogen in the slip zone, we confirmed the previous findings of the first principles results [4] that hydrogen reduces excess energy and thus enables easier slip in the material.

Several problems associated with empirical potentials, such as low transferability, approximate nature due to trial and error, and limited ability for tuning, remain. Part of the outcome of this thesis is to quantify these problems for the MEAM formalism.

1.1 Outline

The investigation into the matter of finding a proper MEAM potential to simulate behavior of stacking faults in zirconium hydrogen solid solutions consists of the following chapters:

- **Review of Literature and Background Information**

This section begins with the analysis of zirconium hydrogen phase diagram and the basic nature of interaction between these two elements. Then a brief review of the empirical potentials and the MEAM formalism would introduce the main topic of this research: creation of the new 2nnMEAM.

- **Testing the MEAM Potential**

First, the basic bulk properties tests for calculating lattice constants, elastic constants, bulk modulus, and the UBER curve were used to gradually introduce the MEAM's ability to handle different zirconium hydride phases. Second, stacking fault tests of different concentrations of dissolved hydrogen in zirconium were performed in order to replicate available first principles results. The first part of the tests was successful, but when it comes to the second part, the MEAM potential was not capable to handle complex changes happening in the material. Furthermore, it will be shown that problems with the MEAM formalism introduced in the previous section would bear heavily on the effort to confirm the first principles results about excess energy during slip in the zirconium hydrogen solid solutions.

- **The formalism and Testing of The Second Nearest-neighbor MEAM (2nnMEAM) Potential**

A number of papers deal with the formalism of the second nearest neighbor

MEAM potentials for different binary alloys. They all describe a general framework and use bulk tests to confirm primarily the basic properties of the binary alloys. At the same time, considerable number of parameters had to be estimated by trial and error. The same principles were used in creating the new 2nnMEAM potential, but this time potential had to simulate more demanding changes in the material associated with deformation tests such as stacking fault. Compared to the MEAM, 2nnMEAM was qualitatively successful. At the same time, 2nnMEAM will be affected by limitations of the MEAM formalism mentioned in the previous sections. We also explore these limitations of our new potential.

- **Discussion**

The results will be compared with DFT results and related to the DHC theory [4,9]. Furthermore, problems and deficiencies of the MEAM formalism will be explained in detail. Future work and potential uses will also be addressed.

Chapter 2

Review of Literature and Background Information

2.1 Zirconium Hydrogen System

Zirconium content in the earth's crust is 0.028 percent which makes it the 19th most abundant element in nature. The main commercial source of zirconium is the silicon mineral, zircon $ZrSiO_4$, found primarily in Australia, Brazil, India, South Africa, Russia and US. With melting point at 1930 °C(3506 °F), good high temperature mechanical properties and thermal conductivity, stability of these properties after irradiation combined with a low neutron capture cross section and high corrosion resistance, it is clear why zirconium is an obvious choice for nuclear industry applications [10].

Hydrogen is abundantly present on Earth and in the Universe. Depending on the thermodynamic state the elemental hydrogen exists in several different forms. On Earth, hydrogen usually exists only as molecules [11]. Due to high reactivity of hydrogen atoms they naturally combine into H_2 molecules. Also, hydrogen has some unique features, namely small atomic size and mass, medium electronegativity and the ability to react with various elements in a wide temperature range. Generally, we can introduce an element and its characteristics by looking at atomic size, nuclear mass and electronegativity. It is immediately clear that having a very small size, the hydrogen atom can easily penetrate an interstitial site in a metal lattice. As a matter of fact, all three charged states of hydrogen, H^- , H^0 , H^+ have rather large radius 2.1Å, 0.529Å, and ≈ 0.25 Å respectively. But, at the same time, electronic calculations have shown that when hydrogen is placed in transition metals 1s orbitals are strongly hybridized with d-orbitals of surrounding atoms. Thus, the ability of

hydrogen to penetrate the narrow interstitial sites in metal lattices is due in part to the flexibility of surrounding electronic states [11]. Hydrogen has a small nuclear mass and medium electronegativity. Because hydrogen has a medium value of electronegativity, it can create a wide range of bonds with different elements. Depending on the electronegativity of the two atoms joined by a bond, a general classification of bonds can be made. The higher the electronegativity difference the more ionic the bond, the lower the difference the more covalent the bond. In reality, more common is a combination of bonds than a pure covalent or pure ionic bond. All of those facts about hydrogen explain in part hydrogen reactivity and high mobility within host element lattice. It has to be stressed that not much is known about the detailed interaction of hydrogen with the host metal atoms [12].

The equilibrium phase diagram for zirconium and hydrogen Fig.2.1 [5] is of the eutectoid type and consists of the following phases:

1. αZr - the hcp terminal (random interstitial) solid solution, $P6_3/mmc$ space group, with maximum hydrogen solubility of 5.9 at.%H at 550 °C. Depicted in Fig.2.2, the Zr hcp lattice has tetragonal and octagonal positions available for hydrogen to occupy, and neutron scattering measurements concluded that hydrogen atoms are located in the tetragonal sites. The hcp basal plane of pure Zr (αZr) is surrounded by tetragonal sites for dissolved hydrogen atoms, as shown in Fig.2.3. The unit cell for a solid solution consists of two Zr atoms in positions (0,0,0) and (2/3,2/3,1/2), and four potential sites for hydrogen atoms on (0,0, $\pm 3/8$) and (2/3,2/3, $\pm 1/7$).
2. βZr - the bct terminal (random interstitial) solid solution, $Im\bar{3}m$ space group, with an eutectoid composition of 37.5at.%H at 550°C, Fig.2.4. Body-centered tetragonal (bct) structure has Zr atoms occupying all bcc positions, but in a tetragonally deformed bcc lattice to accommodate hydrogen atoms on the sides. The unit cell consists of two Zr atoms in (0,0,0) and (1/2,1/2,1/2), while four hydrogen atoms occupy (1/2,0,1/4), (0,1/2,1/4), (1/2,0,3/4), and (0,1/2,3/4) sites.
3. δZr - the fcc δ phase, fluorite structure of the $Fm\bar{3}m$ space group, is the most common hydride with the composition of around $ZrH_{1.6}$. αZr and δZr cover almost the whole area of the phase diagram below eutectoid temperature till

Figure 2.1: Zr-H Phase Diagram [5]

around hydrogen concentration of 1.6 wt.% H, followed by a very narrow zone of pure δ Zr. The unit cell consists of four fcc unit cell Zr atoms, (0,0,0), (1/2,0,1/2), (0,1/2,1/2), (1/2,1/2,0), and the cube with randomly arranged 6 hydrogen atoms in the center off the zirconium fcc lattice with 1/2 of the fcc lattice constant. Both Fig.2.3 and Fig.2.4 depict this arrangement.

4. ϵ Zr - Zuzek et al. [5] described the ϵ hydride as an fct, face-centered tetragonal or distorted fluorite structure, of the $I4/mmm$ space group, which actually represents a bct lattice type. That was repeated in many academic papers, e.g. [8, 13, 14]. Furthermore, experimentally ϵ phase was investigated more as an fcc and fct lattice, than as a stable bct. At room temperature, δ zone and δ and ϵ zone on the phase diagram are rather narrow which means that the full phase transformation from fcc to bct happens due to a slight increase in the hydrogen concentration. The fct ϵ phase, has an axial ratio $c/a < 1$ and the composition of around ZrH_2 . The bct structure is the bcc lattice that is tetragonally distorted, $c/a > 1$ and with two hydrogen atoms on each of the four sides, as depicted in Fig.2.4.

5. γZr - the fct γ metastable phase, of the $P4_2/n$ space group, with ratio $c/a > 1$ and composition of ZrH . Different arrangements of hydrogen atoms inside a slightly tetragonally deformed fcc lattice are depicted in Fig.2.5. One is the plane arrangement where all hydrogen atoms lay in the (110) plane and the other one is with the diamond arrangement where hydrogen atoms occupy tetragonal positions on alternate (110) planes. γZr is the only zirconium hydride that has the stoichiometric composition. δZr and ϵZr have hydrogen compositions in the range of wt.% H of 1.5 and 1.8, respectively.
6. ζZr - the hcp ζ metastable/transient phase has been reported with probable stoichiometric composition Zr_2H in Zircaloy-4 alloys submitted to hydrogen cathodic charging or autoclave corrosion [15]. This hydride has a hexagonal lattice and belongs to the trigonal crystal system with the space group $P3m1$.

Figure 2.2: Zr-H solid solution, αZr [4]

With different concentrations of hydrogen, temperature and cooling rates, the above mentioned phases are created. In all of the equilibrium phases αZr , βZr , δZr , ϵZr the tetrahedral interstitial positions are occupied at random by hydrogen. On the other hand, ordered arrangements of hydrogen are present in metastable γZr , δZr and ϵZr phases cooled below room temperature. γZr is formed

Figure 2.3: Unit cell for Zr-H solid solution (α Zr) and δ hydride ($ZrH_{1.5}$) δ Zr, respectively [4]. In both α Zr and δ Zr only tetrahedral sites were occupied by hydrogen.

Figure 2.4: β Zr bct and δ Zr fcc structure

from hcp α Zr by means of a hybrid process of shear of hcp lattice and a simultaneous diffusional migration of hydrogen. The same process is also responsible for transformation from δ Zr to γ Zr hydride. Electron microscopy examination of hydrides shows that after rapid cooling from above the solvus temperature, precipitates occur at random, often on dislocations and consist mainly of γ Zr. Intermediate cooling produces a mixture of γ Zr and δ Zr, while slow cooling creates untwinned δ Zr hydride [5].

Investigation of hydride locations within the α Zr hcp matrix shows that precipitation of hydrides is predominant along grain boundaries [16]. But, the ratio of intra-granular (inside the grains) hydrides to inter-granular (between grains) hydrides

Figure 2.5: γ Zr fcc plane and diamond arrangement of hydrogen atoms [8]

Phase	Composition, <i>at.%H</i>	Pearson symbol	Space group	Structur-	Prototype
				bericht designation	
α Zr	0 – 5.93	<i>hP2</i>	$P6_3/mmc$	A3	<i>Mg</i>
β Zr	0 – 54.55	<i>cI2</i>	$Im\bar{3}m$	A2	<i>W</i>
δ Zr	56.71 – 66.67	<i>cF12</i>	$Fm\bar{3}m$	C1	<i>CaF_2</i>
ϵ Zr	66.67 – ...	<i>tI6</i>	$I4/mmm$	$L/2_b$	<i>ThH_2</i>
Metastable phase					
γ Zr	50.0	<i>tP6</i>	$P4_{2/n}$		$ZrH_{0.5}$

Table 2.1: Zr-H system phases [5]

depends on the cooling rate and initial sample condition. The same applies to the amount of γ Zr and δ Zr hydrides created in the matrix.

2.2 Atomistic Simulations

2.2.1 Introduction

Atomistic simulation allows us to study material behavior at the atomistic scale by investigating how atoms interact with one another inside the structure. Different phenomena, such as material defects and deformations, require the atomic scale accuracy and understanding of interactions between atoms. The first step of an atomistic simulation involves creating a material structure by means of a set of atomic coordinates, which in case of metals involves creating a crystal lattice and placing atoms on lattice points. Next, the simulation requires an energy functional or potential, that governs how atoms interact. The potential presents the biggest challenge and can be based on classical dynamics (Molecular Dynamics (MD) approach) or quantum mechanics (first-principles tests). The main difference between those two is that latter is based on solution and different approximations of the electronic Schroedinger equation. This is more accurate because, the electronic structure of each atom is analyzed, but must be applied on the smaller number of atoms due to high computational cost and limited computational capabilities available. Major methods are Density Functional Theory (DFT) and Tight Binding (TB). Whereas, the MD approach is based on the simplified mathematical expressions that replaces the electronic degrees of freedom by an effective potential and forces between the nuclei. Without complex electronic structure of each atom MD is able to handle models with higher number of atoms, but with less accuracy [17]. This approach is the focus of this research.

2.2.2 Empirical Atomistic Models

Metallic bonding is characterized by electrostatic forces between an electron cloud of "free" electrons and the positively charged metal ions. Electrons in the cloud are shared among lattice bound positive ions. So, an effective potential should as accurately as possible describe the potential energy of positively charged ions while approximating the electron contribution to the energy as a function of ion positions.

Here we deal with solid metallic systems and the main challenge is for the potential to describe the environment of an atom embedded in the background of valence electrons of the host solid. This valence electron density is effectively described by the Embedded Atom Method (EAM) [1]. Empirical potentials, such as EAM, use a purely

classical description of interactions between atoms which means the introduction of approximations that limit the transferability of the model. An effective empirical potential must satisfy the following critical properties [18]:

1. *Flexibility*: In order to be flexible, a potential has to feature a sufficient range of fitting parameters to match key properties such as, for solids, lattice constants, cohesive energy, elastic properties, vacancy formation and surface energies.
2. *Accuracy*: Fitting parameters enable a potential to be fine-tuned to closely reproduce results of more accurate first-principles methods used as the basis for its creation.
3. *Transferability*: Now the fine-tuned potential should be able to describe structures not included in its fitting data base. On many occasions, this is only possible with qualitative, but not quantitative accuracy.
4. *Computing efficiency*: The potential has to function within limits of available computational resources, handle the system size and timescales of interest efficiently.

2.2.3 Embedded Atom Method [1]

A simplified approach towards the total energy of a solid is to assume that it can be expressed as a sum of all pair interactions between atoms. These interactions would be regarded as independent of one another, so that one bond is not affected by the presence of another bond. In reality, bonds in metals do not follow this simple pair-potential approximation due to many-atom interactions that govern fundamental properties of solids.

Embedded atom method (EAM), a pair functional model, was developed in order to accurately treat metallic systems in terms of their fracture response, surfaces, impurities and alloying additions. The basis for the EAM is the quasiatom, as well as the effective medium theory. Quasiatom is a term that treats the whole atom nucleus or ion, and electron polarization cloud as a single unit. Its energy is a function of the host electron density in which it is immersed. The quasiatom is neutral and unaffected by electric potentials due to charge distributions. Effective medium theory is another approach for calculating the embedding energy of an atom in a host system. The basic idea is to replace the (low-symmetry; imperfect) host by an effective (high-symmetry;

ideal) host consisting of a homogeneous electron gas (jellium) of a density equal to that seen by the atom [1].

Jellium, also known as the uniform electron gas (UEG) or homogeneous electron gas (HEG), is a quantum mechanical model of interacting electrons in a solid. Positive charges (i.e. atomic nuclei) are assumed to be uniformly distributed in the space, therefore the electron density is also uniform in the space. So, without using the crystal structure of a real material we can analyze the effects due to quantum nature of electrons. This model serves as the basis for the EAM form.

In the embedded atom method the energy of the metal, E , is derived from the embedding energy F and an electrostatic pair potential ϕ . The embedding energy is the energy to embed an atom into the local electron density created by the remaining atoms in the system. The EAM [19] takes the form:

$$E = \sum_i F_i \left(\sum_{j(\neq i)} \rho_j^\alpha(R_{ij}) \right) + \frac{1}{2} \sum_{\substack{ij \\ (j \neq i)}} \phi_{ij}(R_{ij}), \quad (2.2.1)$$

where F [eV], the embedding energy, is the function of ρ^α [$\text{\AA}^{-3}$], the spherically averaged electron density, ϕ_{ij} [eV] is the electrostatic pair potential and R_{ij} [$\text{\AA}$] is the distance between atoms i and j . i and j run over all the atoms in the system.

2.2.3.1 The Universal Binding Energy Relation (UBER)

The Universal Binding Energy Relation (UBER) [20] is an analytical relationship where only two equilibrium values for a material, cohesive energy E_{coh} and bulk modulus B , are needed to scale energy E^* and lattice constant a^* for an entire cohesive energy versus lattice constant curve for any crystal to be known. First-principles quantum results do not form a single smooth line, but UBER's analytical relationship fits them very well [21].

MEAM potential requires the exact fit to the UBER curve as a part of its functional form because in MEAM the energy per atom in the reference structure is obtained from UBER [3].

E^* and a^* are two scaled parameters for energy and length:

$$E^* = -\frac{E_{coh}}{E_{coh}^0} \quad (2.2.2)$$

$$a^* = \frac{r_{WS} - r_{WS}^0}{l} \quad (2.2.3)$$

where E_{coh}^0 is the equilibrium cohesive energy, r_{WS} is the radius of a sphere containing the same volume as the average volume per atom, Ω , in the structure:

$$r_{WS} = \left(\frac{3\Omega}{4\pi} \right)^{\frac{1}{3}} \quad (2.2.4)$$

and r_{WS}^0 is this same radius at the equilibrium volume. The length scale parameter l is defined as:

$$l = \sqrt{\frac{E_{coh}^0}{12\pi B r_{WS}^0}}. \quad (2.2.5)$$

where B is the bulk modulus of the crystal.

All these equations lead to the final form of universal function [20]

$$E^*(a^*) = -(1 + a^* + 0.05(a^*)^3)e^{-a^*} \quad (2.2.6)$$

The simplified form of the universal function is given as

$$E^*(a^*) = -(1 + a^*)e^{-a^*} \quad (2.2.7)$$

The difference between two forms of UBER, in Equ.2.2.6 and Equ.2.2.7, is in the higher-order term which has an effect far from equilibrium state.

2.2.4 Modified Embedded Atom Method (MEAM) potential

Dr.M.I.Baskes, the creator of the MEAM potential, started the development process of the MEAM by working on the problem of covalent bonding in silicon [22]. The EAM potential was used as the basis for a new semi empirical formalism with added angle-dependent electron density to successfully model the effects of bond bending. Different metastable phases of silicon were successfully simulated by EAM in terms of the geometry and structure. The problem was that EAM was not able to explain the shear behavior which includes effects such as directionality of bonding and bond bending. This new semi empirical model for silicon was simple and had a straightforward application to alloy systems, although only for calculation of bulk properties such as cohesive energy and lattice constants. The following paper [23] defined the model as the MEAM and applied it to silicon, germanium and their alloys. The main motivation was to create a potential with some physical basis so that different untried geometries and alloys can be investigated with more confidence and for a new potential to be more universal and capable to simulate many phenomena successfully. That is one of the most important properties of empirical potentials called transferability. In [3], Dr. Baskes further improved the MEAM formalism and applied it to a variety of cubic materials (face-centered cubic (fcc), body-centered cubic (bcc) and diamond cubic) and impurities. The MEAM successfully described the elastic behavior and simple defect properties. The screening function was developed and only first-nearest neighbor interactions were considered. Several papers followed, further enhancing the formalism and applicability of the MEAM potential. To mention a few, MEAM for hcp materials [24], MEAM for nickel [25], and most importantly an extension of the MEAM called the Second nearest-neighbor modified embedded atom method potential (2nnMEAM) [2].

2.2.5 Second Nearest-neighbor Modified Embedded Atom Method (2nnMEAM) potential [2]

The MEAM potential was able to reproduce physical properties of many metals with various crystal structures including hcp, diamond cubic, fcc and bcc. All of the tests used to test the MEAM were basic bulk properties tests, where only slight and symmetric changes to the lattice parameters occurred. However, for some bcc metals, MEAM was not able to predict that (111) surface energy is higher than that of the

(100) plane, which had been experimentally confirmed. Also, during the molecular dynamics calculations of bcc metals such as Fe, Cr, Mo, etc., MEAM created a structure more stable than bcc and elastic properties of the newly created structure was quite different compared to the original bcc structure of the material [2].

The MEAM potential was based on nearest-neighbor interactions and for pure elements that simplification had negligible influence on the simulation results for many materials. In pure elements nearest-neighbors completely screen interactions from farther neighbors. Furthermore, the exponential decay of electron density causes the second-neighbor contribution to the energy (and elastic constants) to be comparatively small.

But when it comes to alloys, the interaction between atoms depends upon distances and upon the species of the interacting atoms. Also, the first-nearest neighbors does not effectively screen the second-neighbor interactions, thus they cannot be neglected [2].

Furthermore, in the bcc structure, there is only 15% difference between second and first nearest-neighbor distance, so even strong first-neighbor screening function may not be enough to prevent the second nearest-neighbor interactions. Original MEAM fails to reproduce the surface energies of low index surfaces (the Miller indices consist of small numbers such as 0 or 1). surfaces in the correct order and that might be caused by considering only the nearest-neighbor interactions [2].

Here, the complete formalism of the 2nnMEAM will be presented. MEAM and 2nnMEAM share the same basic equations with 2nnMEAM having improved screening function compared to the MEAM [3], slightly modified partial electron density from MEAM for nickel [25] and longer range interactions than first nearest neighbor.

The total energy, E , of a system is defined the same way in EAM [1] and MEAM [3]. There is only a slight difference in the notation and the background electron density $\bar{\rho}_i$ is different to the one in EAM. The total energy, E , of a system of a single type of atoms in MEAM [3] is described as by an approximate form:

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(R_{ij}) \right], \quad (2.2.8)$$

where F is the embedding energy required to embed an atom into the background

electron density at site i , $\bar{\rho}_i$, and $\phi_{ij}(R_{ij})$ is the pair interaction between atoms i and j at a distance R_{ij} .

The embedding function has the form:

$$F(\bar{\rho}) = AE_c \left(\frac{\bar{\rho}}{\bar{\rho}^o} \right) \ln \left(\frac{\bar{\rho}}{\bar{\rho}^o} \right), \quad (2.2.9)$$

where A is an adjustable parameter (a constant determined from the fcc-bcc energy difference derived from phase diagrams [3]), E_c [eV] is the sublimation energy, and $\bar{\rho}^o$ [$\text{\AA}^{-3}$] is the background electron density for a reference or equilibrium structure.

In the EAM [1], $\bar{\rho}_i$ is given by a linear superposition of spherically averaged atomic electron densities, while in the MEAM, $\bar{\rho}_i$ is augmented by angular dependent terms [25]. Therefore in MEAM the background electron density $\bar{\rho}_i$ consists of spherically symmetric partial electron density $\rho_i^{(0)}$ and angular contributions $\rho_i^{(1)}$, $\rho_i^{(2)}$, $\rho_i^{(3)}$, where $\rho_i^{(3)}$ was chosen in order to make the partial electron densities orthogonal Legendre functions [26, 27].

$$(\rho_i^{(0)})^2 = \left[\sum_{j(\neq i)} \rho_j^{a(0)}(R_{ij}) \right]^2 \quad (2.2.10)$$

$$(\rho_i^{(1)})^2 = \sum_{\alpha} \left[\sum_{j(\neq i)} (R_{ij}^{\alpha}/R_{ij}) \rho_j^{a(1)}(R_{ij}) \right]^2 \quad (2.2.11)$$

$$(\rho_i^{(2)})^2 = \sum_{\alpha, \beta} \left[\sum_{j(\neq i)} \frac{R_{ij}^{\alpha} R_{ij}^{\beta}}{R_{ij}^2} \rho_j^{a(2)}(R_{ij}) \right]^2 - \frac{1}{3} \left[\sum_{j(\neq i)} \rho_j^{a(2)}(R_{ij}) \right]^2 \quad (2.2.12)$$

$$(\rho_i^{(3)})^2 = \sum_{\alpha, \beta, \gamma} \left[\sum_{j(\neq i)} \frac{R_{ij}^{\alpha} R_{ij}^{\beta} R_{ij}^{\gamma}}{R_{ij}^3} \rho_j^{a(3)}(R_{ij}) \right]^2 - \frac{3}{5} \sum_{\alpha} \left[\sum_{j(\neq i)} \frac{R_{ij}^{\alpha}}{R_{ij}} \rho_j^{a(3)}(R_{ij}) \right]^2. \quad (2.2.13)$$

Here, $\rho_j^{a(h)}$ represent atomic electron densities from j atom at a distance R_{ij} from site i . R_{ij}^α is the α component of the vector between atoms j and i , and α , β and γ summations are each over the three coordinate directions. The functional forms for the partial electron densities were chosen to be translationally and rotationally invariant and equal to zero for crystals with cubic symmetry. The forms chosen in Eqs.(2.2.10)-(2.2.13) are related to powers of the cosine of the angle between groups of three atoms [25]. Finally, atomic electron densities are assumed to decrease exponentially, i.e.,

$$\rho^{a(h)}(R) = \exp \left[-\beta^h (R/r_c - 1) \right], \quad (2.2.14)$$

where the decay lengths, β^h , are constants. To obtain the background electron density from the partial electron densities we make the assumption that the angular terms are a small correction to the EAM [25].

There are several ways to combine the partial electron densities to get the total background electron density. Before we continue with our presentation we will first show what are the options and what is their effect on calculations [28].

Angular dependences are combined into one term in the following form:

$$\Gamma = \sum_{h=1}^3 t^{(h)} \left(\frac{\rho^{(h)}}{\rho^{(0)}} \right)^2 \quad (2.2.15)$$

where $t^{(h)}$ are constants [3, 25]. The background density is then calculated from the following equation:

$$\bar{\rho} = \rho^{(0)} G(\Gamma) \quad (2.2.16)$$

where $\Gamma = 0$ in the case where there is no angular dependence. In order to recover the original EAM form we need $G(0) = 1$.

There are three forms of the $G(\Gamma)$ function [25]:

$$G(\Gamma) = \sqrt{1 + \Gamma} \quad (2.2.17)$$

$$G(\Gamma) = \exp(\Gamma/2) \quad (2.2.18)$$

$$G(\Gamma) = \frac{2}{1 + \exp(-\Gamma)} \quad (2.2.19)$$

In the initial MEAM formalism Eq.(2.2.17) was used and it is not suitable when any of the $t^{(h)}$ values are less than zero because it produces imaginary electron densities when $\Gamma < -1$. So Eq.(2.2.18) and (2.2.19) were used and it was Eq.(2.2.19) that turned out to be the most versatile and able to reproduce the most of the experimental data. That is why that form of the $G(\Gamma)$ function will be used here [25].

As mentioned in the paragraph 2.2.3.1, the MEAM total energy, Eq.2.2.8, as a function of the nearest-neighbor distance R , requires the exact fit with the universal equation of state (UBER):

$$F(\bar{\rho}^o) + \frac{1}{2} \sum \phi(R) = E^u(R) = -E_{coh}(1 + a^*)e^{-a^*}, \quad (2.2.20)$$

and from there the pair potential $\phi(R)$ between two atoms separated by a distance R can be determined as

$$\phi(R) = (2/Z_1)\{E^u(R) - F[\bar{\rho}^o(R)]\} \quad (2.2.21)$$

where Z_1 is the number of the nearest neighbors.

This completes the MEAM formalism, which is the same for the 2nnMEAM, apart from the details of the screening function.

2.2.6 Screening Function

The screening function is a many-body function that places additional limitation on the interactions between atoms in the MEAM. The original screening function [3] introduced a discontinuity which led to infinite forces. On the other hand, the new implementation, described below, was proven to work well [25, 29]. Between two atoms, i and j , the screening function S_{ij} is defined as the product of the screening factors, S_{ikj} , due to all other neighbor atoms k :

$$S_{ij} = \prod_{k \neq i,j} S_{ikj} \quad (2.2.22)$$

By multiplying the atomic electron densities and the pair potential by S_{ij} , screening is introduced in the interactions. For $S_{ij} = 1$ interactions between atoms i and j are unscreened and if $S_{ij} = 0$ they are completely screened. The screening function depends on the positions of all of the other atoms in the system.

S_{ijk} is defined by an ellipse as presented on the Fig. 2.6:

$$x^2 + \left(\frac{1}{C}\right)y^2 = \left(\frac{1}{2}r_{ik}\right)^2 \quad (2.2.23)$$

where the parameter C is defined as:

$$C = \frac{2(X_{ij} + X_{jk}) - (X_{ij} + X_{jk})^2 - 1}{1 - (X_{ij} + X_{jk})^2}, \quad (2.2.24)$$

where $X_{ij} = (r_{ij}/r_{jk})^2$ and $X_{jk} = (r_{jk}/r_{ik})^2$. The r_s are the distances between the respective atoms.

Screening factor S_{ijk} is chosen to be a smooth function of C :

$$S_{ijk} = f_c \left[\frac{C - C_{min}}{C_{max} - C_{min}} \right] \quad (2.2.25)$$

where C_{min} and C_{max} are the limiting values of C and the smooth cutoff function f_c is:

$$f_c(x) = \begin{cases} 1, & x \geq 1, & \text{unscreened} \\ [1 - (1 - x)^4]^2, & 0 < x < 1 & \text{partially screened} \\ 0, & x \leq 0, & \text{screened} \end{cases} \quad (2.2.26)$$

Figure 2.6: Screening function diagram of screening of atom k and atom i by atom j . If atom j is inside the small ellipse defined by C_{min} then it is fully screening the interaction of atoms i and k . When atom j is outside the small ellipse and in between the small C_{min} and the big C_{max} , then atom j only partially screens their interaction. No screening occurs when atom j is outside the big ellipse C_{max} .

C_{min} and C_{max} are determined by analyzing FCC and BCC structures [25]. Let us consider atom j equidistant from atoms i and k , $X_{ij} = X_{jk}$, as seen in Fig.2.7. Those three atoms then represent an equilateral triangle of the three nearest neighbors in the FCC structure and it yields $C = 3$, Fig.2.7b. On the other hand, i and k are second neighbors in the BCC structure with atom j a first neighbor to i and k ,

$C = 2$, Fig. 2.7a. These two cases define the limits for no screening. Therefore we require $C > 3$ for atoms i and k to be unscreened, $S_{ijk} = 1$ and for $C < 2$ for atoms i and k to be completely screened, $S_{ijk} = 0$. Generally used values for C_{min} and C_{max} are 2.0 or 0.8 and 2.8, respectively.

Figure 2.7: a) $C < 2$ limit for complete screening of atoms i and k by atom j shown on bcc lattice b) $C > 3$ limit for no screening of atoms i and k by atom j shown on fcc lattice

Also, a radial cutoff function is applied to the atomic electron densities and the pair potential in the form of $f_c [(r_c - r)/\Delta r]$, where r_c is the cutoff distance and Δr defines the cutoff region.

2.2.6.1 Adapting The New Screening Function and Analysis of 2nn MEAM Parameters

The basic formalism of the MEAM and 2nnMEAM is the same, except for the pair potential and the screening function parameters. The original MEAM [3] had a nearest neighbor screening function in order to limit interactions to the first neighbors and the limiting values of the C parameter were chosen as $C_{min} = 2.0$ and $C_{max} = 2.8$. Now, those limiting values have to be changed to allow for second nearest-neighbor

interactions to be included in the energy calculations. For fcc and bcc C_{min} has to be lower than 1.0 and 2.0, respectively [2].

For a given reference structure, and a fixed value for C_{max} , we can assume a value for C_{min} and have the screening become a constant [2]. Then, energy per atom in a reference structure can be expressed as follows:

$$E^u(R) = F [\bar{\rho}^0(R)] + (Z_1/2)\phi(R) + (Z_2S/2)\phi(aR) \quad (2.2.27)$$

where Z_1 and Z_2 is the number of first and second nearest-neighbor atoms, respectively, and a is the ratio between the second nearest-neighbor distance and first nearest-neighbor distance. Also, the background electron density has to be adapted for longer interactions. For a bcc or fcc reference structure, it is calculated as a function of first nearest-neighbor distance R as:

$$\bar{\rho}^0(R) = Z_1\rho^{a(0)}(R) + Z_2S\rho^{a(0)}(aR), \quad (2.2.28)$$

new pair potential $\psi(R)$ is introduced and Eq. (2.2.27) can be written again as:

$$E^u(R) = F [\bar{\rho}^0(R)] + (Z_1/2)\psi(R) \quad (2.2.29)$$

where

$$\psi(R) = \phi(R) + (Z_2S/Z_1)\phi(aR). \quad (2.2.30)$$

$\psi(R)$ is calculated from Eq. (2.2.29) and the pair potential $\phi(R)$ is calculated from:

$$\phi(R) = \psi(R) + \sum_{n=1} (-1)^n (Z_2S/Z_1)^n \psi(a^n R). \quad (2.2.31)$$

Eq.(2.2.31) is purely a mathematical relationship between ϕ and ψ , and the summation is performed until the correct value of energy is obtained for the equilibrium reference structure [2].

For the bcc structure, in the case of $C_{min} < 0.47$, even the third nearest-neighbor interactions are not completely screened for the reference structure. In case of element Fe ($C_{min} = 0.16$) the contribution to the potential energy from them is very small, as well as the error in the potential energy calculations if they are ignored. So, in order to avoid that error all together, C_{min} should remain larger than 0.47 and then third nearest-neighbor interactions are completely screened [3].

Table 2.2 shows how different parameters influence physical properties of bcc elements. The plus sign means that the effect on physical properties is significant, the minus means minor effect and no sign means no effect. C_{11} and C_{12} are dependent of each other when bulk modulus B value is given [2].

	A	$\beta^{(0)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$	C_{min}
C_{11} and C_{12}	+	+		-		+
C_{44}	+	+		-		+
$E_{(surf)}$	+	-	+	-	-	-
$\Delta E_{bcc \rightarrow fcc}$	+	+				+
$\Delta E_{fcc \rightarrow hcp}$	+	+			+	+

Table 2.2: Table of parameter influence on physical properties for bcc elements. The plus sign means that the parameter has a strong influence on the property, the negative sign means a weak influence and no sign means no effect.

One of the approaches for the fitting procedure is to first determine values of A , $\beta^{(0)}$, C_{min} , and $t^{(3)}$ by fitting to elastic constants (C_{11} , C_{44}) and structural energy differences ($\Delta E_{bcc \rightarrow fcc}$, $\Delta E_{fcc \rightarrow hcp}$). But, it is not always possible to fit all of those properties with four parameters. Elastic constants are fitted exactly and structural energies as close as possible. After that, $t^{(1)}$ and $t^{(2)}$ are determined from surface energies and heat of vacancy formation. As a test the order of the low index surfaces energies can be checked and one can also confirm what is the most stable phase of the element in question [2].

2.2.7 Application to Binary Alloy Systems [3]

When EAM was applied to impurity and alloy systems, experimental values of dilute heats of solution were used to scale the electron density and determine the unlike-atom pair potential. A geometric mean was assumed between the like atom potentials. In MEAM we consider an equiatomic binary intermetallic alloy system ij , where each i atom has only j neighbors and vice versa. Examples of these crystal structures are B1 NaCl and B2 CsCl, with 6 and 8 neighbors respectively. Since they are cubic and have a center of symmetry, the total energy per atom (atom represented by one half of atom i and one half of atom j , $E_{ij}^u(R)$ is given as [3]:

$$E_{ij}^u(R) = \frac{1}{2} \left\{ F_i \left[Z_{ij} \rho_j^{a(0)}(R)/Z_i \right] + F_j \left[Z_{ij} \rho_i^{a(0)}(R)/Z_j \right] + Z_{ij} \phi_{ij}(R) \right\} \quad (2.2.32)$$

where Z_{ij} is the number of nearest neighbors to an i or j atom. In order to solve for the pair potential we use UBER with $E_{ij}^0 = (E_i^0 + E_j^0)/2 - \Delta_{ij}$, $\alpha_{ij} = (\alpha_i + \alpha_j)/2$, and R_{ij} from the atomic volume $\Omega_{ij} = (\Omega_i + \Omega_j)/2$. The enthalpy of mixing Δ_{ij} is obtained from experimental or approximate calculated values. Also, it is assumed that partial electron density weights depend only on the embedded atom type and not on the type of the atom contributing to the density. Furthermore, no scaling of electron densities is performed, which was the case as mentioned above. When electron densities are not scaled, every type of atom has equilibrium separation electron density. If the intermetallic energy is known we do not need these approximations, and to produce more detailed calculations the heats of solution should be used to scale the densities [3].

A more general procedure of creating binary alloy 2nnMEAM potentials from previously developed MEAM potentials (see, for example, reference [7, 30–33]) will be used to develop a new zirconium hydrogen 2nnMEAM for simulation of stacking fault energy in their different solid solutions.

2.2.8 Testing procedure for MEAM potential

Generally two groups of tests have been performed here. The first group of tests deals with the bulk properties of pure zirconium and its hydrides. Those tests do not break the symmetry of the structure, do not create new phases by rearrangement

of atoms or by changing the bonds between atoms and do not deviate far from the original material structure. Basically, the potential has to handle only slight changes in a fully relaxed and equilibrated structure, for which it was designed in the first place. These tests include: cohesive energy E_{coh} , lattice constants, $a, c, c/a$, elastic constants C_{ij} , and bulk modulus, B . The second group of tests is used to prove the suitability of available MEAM potentials in dealing with problems more closely related to hydride embrittlement in zirconium. Those are deformation tests that primarily focus on how a specifically tuned potential is handling a complex environment of bond breaking/formation, phase transformations and the overall ability to maintain the stability of the structure between equilibrium states during sliding between atomic planes. The potential has to simultaneously fit both phases as well as their interfaces in the slip zone. Especially, the unstable stacking fault energies are sensitive to differently tuned potentials because atoms move toward smaller interatomic distances away from the equilibrium structure where the potential was developed [34]. For these tests the work of Udagawa et al. [4], later referred to as DFT results, was used to compare excess energy during shear for pure zirconium and zirconium hydrogen solid solutions with different hydrogen concentrations. Udagawa et al. used pure hcp zirconium and started adding hydrogen atoms close to the slip plane, and therefore created three stacking fault energy curves for 0, 0.125 and 0.5 ratio of number of hydrogen atoms to zirconium atoms close to slip plane. This is analogous to creating a zirconium hydrogen solid solution platelet in between two perfect pure zirconium crystals [4].

A minimum of 12 atomic layers of zirconium are needed to create a crystal with a sufficient distance from the top and the bottom surfaces to the slip plane in the middle of the crystal such that their influence on the slip plane is negligible. Then the crystal is placed in pseudo vacuum and the full relaxation of the structure is performed. When such a crystal is cut into two parts, Fig.2.8, by a single plane (defect plane) and subjected to a relative slip displacement $\vec{f}$ parallel to the plane, the reconstructed crystal will have excess energy $\Delta E_{ex}(f)$. The gamma (γ) surface or generalized stacking fault energy is the excess energy associated with arbitrary slip displacement along the plane. It is the energy barrier to slip displacement and governs dislocation motion and dislocation emission around the crack tip. Surface energy and γ surface energy are key factors in the analysis of ductile/brittle behavior of solid materials and therefore they are important tests of any interatomic potential.

The parameter $\theta = H/Zr$, is the ratio of the number of H atoms to the number of Zr atoms in the slip plane zone. The nearest zirconium layer above the slip plane and the nearest one below it, Fig. 2.8, define the slip plane zone. After each slip, relaxation for Zr atoms in the slip plane zone was restricted to the direction perpendicular to the defect plane, while all the other atoms were fully relaxed. That way of relaxation of atoms maintains zero normal stress in the defect plane and corresponds to a relaxed shear [4].

Figure 2.8: Zirconium hydrogen solid solution simulation box for simulation of the generalized stacking fault energy.

The excess energy map (γ surface) by a slip vector $\vec{f}$ in the defect plane, is given as follows:

$$\gamma(\vec{f}) = \frac{\Delta E_{ex}}{A_{slip}}, \quad (2.2.33)$$

$$\Delta E_{ex}(\vec{f}) = E_{tot}^{slip}(\vec{f}) - E_{tot}^{orig}, \quad (2.2.34)$$

where $\Delta E_{ex}(\vec{f})$ is the excess energy and $E_{tot}^{slip}(\vec{f})$ and E_{tot}^{orig} are total energies of the slipped and perfect crystal, respectively. A_{slip} is the area of the cross-section that slip plane creates in the simulation box.

In our case the Zr hcp basal plane was used to calculate the excess energy and the slip displacement vector $\vec{f}$ was along the low energy path (LEP), which requires the least energy for a displacement to take place. For the hcp basal plane, the LEP is along the $(01\bar{1}0)$ direction. In Fig. 2.9 a typical excess energy (stacking fault energy) curve is shown. The starting and ending configuration is a fully relaxed structure connected by a stacking fault energy curve that represents the energy cost of rigidly shifting two semi-infinite blocks of crystal on the specific plane and along a specific vector [35]. The unstable stacking energy γ_{US} is the highest energy barrier on the graph that the system will have first to pass in order to complete the slip.

Figure 2.9: The pure zirconium slip without any relaxation of the crystal structure done with the MEAM.

DFT results, presented in the following section, show that in the Zr hcp basal plane, γ_{US} was lowered with increase of hydrogen concentration. The shape of the curve was maintained for lower concentrations. Higher hydrogen content, on the other hand, completely changes the shape, and γ_{US} goes from positive to negative.

Chapter 3

Testing MEAM potential

3.1 Introduction

The above mentioned first-neighbor MEAM created by Dr.Baskes [36] will first be tested on pure Zr , then on the following zirconium hydrides: ZrH , $ZrH_{1.5}$, and ZrH_2 . For each crystal structure full relaxation (minimization of the forces within the crystal lattice) was performed in order to compare the lattice constants to experimental results. The minimization style is the Polak-Ribiere version of the conjugate gradient (CG) algorithm, and the software is LAMMPS [6]. Second, a pressure-volume test was performed. In LAMMPS the simulation box was created by multiplying a unit cell in all three main directions, x, y and z. By changing the hydrostatic pressure inside the simulation box we measure the change of the volume which is allowed to dilate/contract with all three diagonal components of the pressure tensor coupled together. Therefore, box dimensions are coupled and change by the same percentage every time step during the relaxation. The bulk modulus B was calculated from the slope of the pressure-volume line, $k = \left(\frac{dP}{dV}\right)_{V_0}$, by the equation:

$$B = -V_0 k = -V_0 \left(\frac{dP}{dV}\right)_{V_0}. \quad (3.1.1)$$

Third, elastic constants are calculated in LAMMPS and compared with test results available in the literature. Then, the bulk modulus is calculated from those elastic constants and compared to the result from the pressure-volume diagram test.

3.2 MEAM potential

3.2.1 Pure Zr

The MEAM potential in LAMMPS was used to calculate pure Zr hcp crystal structure parameters: lattice constants $a = 3.234$ Å and $c = 5.13$ Å, and cohesive energy $E = 6.36$ eV/atom. Those values are almost the same as the experimental results in Y. Kim et al. [31] (see Table 3.1).

	a [Å]	c [Å]	c/a	E
ZrH MEAM	3.234	5.13	1.586	6.36
Y. Kim et al. [31]	3.231	5.148	1.593	6.36

Table 3.1: Table of pure Zr lattice constants and cohesive energy

Figure 3.1: Pure Zr MEAM pressure-volume diagram

For the fully relaxed volume $V_0 = 2511.2428$ Å³ and the slope $k = \left(\frac{dP}{dV}\right)_{V_0} = -0.0387$ from Fig. 3.1 the predicted bulk modulus is $B = -V_0 k \approx 97.2$ GPa. That is close to 96.8 GPa from [31]. Bulk modulus for hcp pure Zr from elastic constants is given as follows [37]:

$$B = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + \frac{1}{2}C_{33}). \quad (3.2.1)$$

Elastic constants calculated in LAMMPS for pure Zr are presented in the Table 3.2, together with the calculated bulk modulus. Elastic constants do not match, although the bulk modulus result is almost the same, as well as the lattice parameters and cohesive energy. MEAM potential is based on the fcc lattice and not on the hcp, which is the equilibrium structure for pure Zr. After full relaxation of the pure Zr hcp lattice MEAM changes the stacking of layers in hcp and therefore elastic constants do not match the experimental results.

	C_{11} [GPa]	C_{12} [GPa]	C_{13} [GPa]	C_{33} [GPa]	C_{44} [GPa]	C_{66} [GPa]	B[GPa]
ZrH MEAM	112.85	92.89	79.79	144.629	10.87	9.97	97.2 ⁵
Y. Kim et al. [31]	151.5	71.8	66.1	160.6	34.1	39.9	96.8

Table 3.2: Table of pure Zr elastic constants

3.2.2 Gamma (γ) ZrH

C. Domain et.al [8] examined various arrangements of H atoms on tetragonal positions inside the fcc or fct crystal structure, Fig.2.5, and concluded that the planar arrangement of H atoms in the (110) plane in the fct $c/a = 1.1$ structure is more stable than the same arrangement of H atoms in the fcc crystal lattice. Furthermore, the planar fct has lower formation energy than the diamond fct. The conclusion is that H atoms prefer the planar arrangement to that of the diamond (3D) arrangement.

The unit cell for the γ hydride, ZrH, was replicated in x, y, z direction three times and a simulation box with 216 atoms was created. The full relaxation of the structure was performed which allows the simulation box to relax in any of the three main directions without any constraints. The purpose for that is to find the most stable structure, with the lowest cohesive energy at zero pressure. In Table 3.3, results for the diamond ZrH lattice constant calculated by the MEAM match almost exactly the first principles results from Domain et al. [8]. On the other hand, for the planar

⁵Calculated from Eq.3.2.1

arrangement of H atoms, according to the MEAM, we get different lattice constants compared with first principles results, but with lower cohesive energy E_{coh} than the diamond ZrH, which confirms the first principles conclusions from [8] that planar arrangement is more stable. Cohesive energy is the difference between energy of free atoms and crystal energy of those atoms. It is the energy necessary to decompose the crystal structure into single atoms. The lower (i.e. the more negative) the cohesive energy, the more stable the crystal structure.

	MEAM ZrH		DFT [8]		
	DIAMOND	PLANAR	DIAMOND	PLANAR	
structure	fcc	fct	fcc	fcc	fct
E_{coh} [eV/atom]	-3.23	-4.47	-	-	-
a [Å]	4.7574	4.436	4.77	4.75	4.58
c [Å]	-	5.545	-	-	5.04
c/a	-	1.25	-	-	1.1

Table 3.3: Lattice constants and cohesive energy for fully relaxed γ ZrH, with different arrangement of H atoms, calculated with the MEAM and compared with DFT results

Figure 3.2: ZrH diamond pressure-volume diagram

ZrH diamond structure is the reference structure in MEAM and was used for calculation of elastic constants in LAMMPS and bulk modulus from the pressure-volume diagram. For the equilibrium volume $V_0 = 2932.8715\text{\AA}^3$ and the slope $k = (\frac{dP}{dV})_{V_0} = -0.02216$, from Fig. 3.2, bulk modulus is $B = 64.99\text{GPa}$. Bulk modulus for fcc ZrH from elastic constants is given from [38]:

$$B = \frac{1}{3}[C_{11} + 2(C_{12})] \quad (3.2.2)$$

Elastic constants calculated in LAMMPS for ZrH diamond structure are presented in the Table 3.4.

	$C_{11}[\text{GPa}]$	$C_{12}[\text{GPa}]$	$C_{44}[\text{GPa}]$	$B[\text{GPa}]$
ZrH MEAM	125.48	35.73	10.83	65.01

Table 3.4: Table of ZrH diamond structure elastic constants calculated in LAMMPS with the MEAM potential

Survey of available papers on zirconium hydrides shows no data for ZrH fcc diamond cubic lattice in terms of elastic constants and bulk modulus.

3.2.3 Epsilon ϵ Hydride

For the ϵ hydride ZrH_2 , two crystal structures are suggested by the DFT results of Zhang et al. [13]. The first one is the fct structure with the space group $I4/mmm(No.139)$, which is stable at ambient conditions. The second is the metastable fcc fluorite structure with the space group $Fm\bar{3}m(No.225)$.

Both DFT references [8] and [13] investigated the ϵ hydride, ZrH_2 . The results of Domain et al. [8] were compared to the MEAM results for both fcc and fct structures and presented in Table 3.5. Fcc was chosen because lattice constant a is almost the same in DFT and MEAM, while, on the other hand, fct results have different lattice constants and c/a ratios.

For the fully relaxed volume $V_0 = 3041.1446\text{\AA}^3$ and the slope $k = (\frac{dP}{dV})_{V_0} = -0.04265$, from Fig. 3.3, bulk modulus is $B = 129.7\text{GPa}$. DFT results for the fcc ZrH_2 of Zhang et al. [13] reported $B = 133\text{GPa}$.

	MEAM		DFT [8]	
structure	FCC	FCT	FCC	FCT
# atoms	324	162	-	-
E_{coh} [eV/atom]	-4.08	-4.184	-	-
a [Å]	4.829	3.415	4.82	5.01
c [Å]	-	4.829	-	4.44
c/a	-	1.414	-	0.886

Table 3.5: The MEAM results for the fully relaxed ϵ ZrH_2 calculated in LAMMPS and compared with DFT

Figure 3.3: The MEAM fcc ZrH_2 Pressure-Volume diagram

Elastic constants for the MEAM fcc ZrH_2 calculated in LAMMPS are presented and compared with DFT results from [13] in Table 3.6.

Zhang et al. [13] have almost the same results in terms of lattice constants from the first principles and use the same unit cell, but the elastic constants do not match. The bulk modulus, though, is similar to the first principles result.

	C_{11} [GPa]	C_{12} [GPa]	C_{44} [GPa]	B [GPa]
MEAM	229.04	80.27	22.55	129.86 ⁶
Zhang et al. [13]	82.6	159.7	-19.5	133

Table 3.6: Table of the MEAM ZrH_2 elastic constants

3.2.4 Delta δ $ZrH_{1.5}$ Hydride

δ hydride $ZrH_{1.5}$ was assumed to be cubic, with zirconium atoms in the fcc arrangement and six hydrogen atoms placed inside on tetragonal positions. Two tetragonal positions on a diagonal of the cube are vacant, Fig.2.4. This is an approximation, because in reality hydrogen atoms move inside the fcc box and randomly occupy the six out of eight available tetragonal positions. This model of the δ hydride $ZrH_{1.5}$ was used in many papers ([39], [13], [8]) and the approximation about randomness was not treated in more detail.

	MEAM	DFT [8]	
structure	fcc	fct	fcc
# atoms	270	-	-
E_{coh} [eV/atom]	-3.81	-	-
a [Å]	4.8	5.04	4.79
c [Å]	4.78	4.25	-
c/a	-	0.843	-

Table 3.7: The MEAM results calculated in LAMMPS for the δ $ZrH_{1.5}$ compared with first principles results

There is a slight difference between c and a lattice constants calculated by the MEAM, Table 3.7, and they match closely DFT results in [39] and [8]. We assume that c and a are equal and the crystal structure remains fcc.

For the equilibrium volume $V_0 = 2987.6452\text{\AA}^3$ and the slope $k = \left(\frac{dP}{dV}\right)_{V_0} = -0.030463$, from Fig.3.4, bulk modulus is $B = 91\text{GPa}$. Compared to the DFT results [39] in Table 3.8 there is a big difference in the bulk modulus values.

⁶Calculated from Eq.3.2.2

Figure 3.4: The MEAM fcc $ZrH_{1.5}$ pressure-volume diagram

Elastic constants for fcc $ZrH_{1.5}$ calculated in LAMMPS with the MEAM are presented in Table 3.8.

	C_{11} [GPa]	C_{12} [GPa]	C_{44} [GPa]	B[GPa]
ZrH MEAM	177.97	57.72	17.57	97.8 (Equ.3.2.2)
J.Blomqvist et.al [39]	108	139	51	128

Table 3.8: δ hydride ($ZrH_{1.5}$) elastic constants and bulk modulus

The bulk modulus is now calculated from the elastic constants from Table 3.8. J.Blomqvist et.al [39] have almost the same results in terms of lattice constants from first principles and use the same unit cell, but elastic constants and bulk modulus do not match.

3.2.5 Basal plane shear - comparison with DFT [4]

The generalized stacking fault energy along the low energy path for the hcp Zr basal plane is shown in Fig.3.5. Here the MEAM potential will be applied in order to test its ability to reproduce these first principles results. Details of the tests were explained in Section 2.2.8. We will demonstrate several shortcomings of the original MEAM potential that we hope to rectify in developing 2nnMEAM model.

Figure 3.5: DFT prediction for gamma surface energy of the ZrH solid solution for the basal plane low energy path [4]. y axis is the excess energy [J/m²] and x axis is increments of one third of the $\langle 01\bar{1}0 \rangle$ distance on the basal plane of the hcp lattice. Hydrogen is in the slip zone and during deformation, depending on the hydrogen concentration, creates different hydride-like configurations with zirconium.

The MEAM prediction for basal shear for pure Zr is presented in Fig.3.6. First, the MEAM potential is not able to maintain a perfect hexagonal lattice. After the full relaxation, and partially due to the influence of the vacuum on the top and bottom layers of the crystal, perfect stacking order of A-B-A-B is changed into layers A-B getting closer to each other and at the same time B-A layers getting separated farther from each other, Fig.3.7. Slip plane cuts the crystal in the middle of the B-A zone, thus during the slip atoms in layers B and A react less intensely. That is why the "norelaxation" stacking fault curve in Fig.3.6 has no distinct energy peak at the value of the unstable stacking fault. Due to increased distance, the excess energy values around the maximum value are less different and the curve is flattened. Second, the MEAM potential is not capable to handle the hcp structure during the fully relaxed slip because MEAM was based on the fcc Zr as a lowest energy structure. After each slip and consequent relaxation, atoms create more stable cubic like groups, thus breaking the hcp structure. The sudden drop in excess energy on the fully relaxed curve presents the loss of stability, manifested in the rearrangement of atoms into

a different local structures that is more stable than hcp according to the MEAM potential, Fig.3.6.

Figure 3.6: The MEAM basal shear with and without relaxation, $\theta = 0$. The left y-axis is for the fully relaxed curve, and the right y-axis for unrelaxed.

In Fig.3.8 two curves are presented, one for the relaxed and the other for the unrelaxed shear of the pure zirconium hcp structure with just one hydrogen atom added in the slip zone. The ratio between the number of hydrogen and zirconium atoms in the slip zone is $\theta = 0.0625$. It is obvious by looking at the unrelaxed curve that the hcp structure has been deformed and after the full relaxation it has lost its symmetry. Therefore, there is no periodicity for the unrelaxed curve, even though this should be the case. Bonding between zirconium and hydrogen atoms in the slip zone is stronger than the bonds between nearest neighbors of zirconium atoms. Zirconium atoms located around a hydrogen atom are rearranged to accommodate that bonding. That leads to the problems with the relaxed shear curve. Due to the fact that hcp is not the equilibrium structure for the MEAM potential, one hydrogen atom changes the structure more after each relaxed shear step. So much so, that after the eleventh step, during the slip of 30 steps, the relaxation process did not even converge to a solution. It is not surprising that this problem persists for two hydrogen atoms ($\theta = 0.125$) and eight hydrogen atoms ($\theta = 0.5$) in the slip area. The MEAM potential

Figure 3.7: The distortion of the hcp stacking in the MEAM

effectively relaxes the starting hcp structure, with some loss of symmetry for the $\theta = 0.125$ case. What happens after each slip is that after each relaxation atoms rearrange themselves away from the hcp into a lower energy structure. For those two cases, only the unrelaxed curves are presented on Fig.3.9 and on Fig.3.10, respectively. Both curves are periodic, but are very rough and discontinuous. Sudden changes and peaks reflect instability in the structure and lack of equilibrium of forces on atoms.

That leaves only the pure zirconium relaxed curve from the MEAM potential for comparison with the DFT results. And, even the pure hcp structure, without any hydrogen atoms, is not stable during the slip and relaxation of Zr atoms, resulting in a sudden drop of the excess energy, Fig.3.11.

The MEAM proved to be a versatile empirical potential capable of simulating the basic bulk properties of a variety of different zirconium phases with different crystal structures with reasonable accuracy. However, it is not capable of reproducing the DFT results for slip. Since our aim here is to simulate the stacking fault energy of

Figure 3.8: The MEAM basal shear with and without relaxation, $\theta = 0.0625$. The left y-axis is for the fully relaxed curve, and the right y-axis for unreleased.

Figure 3.9: The MEAM basal shear with and without relaxation, $\theta = 0.125$.

different zirconium hydride solid solutions, a new 2nnMEAM has to be created.

Figure 3.10: The MEAM basal shear with and without relaxation, $\theta = 0.5$.

Figure 3.11: The MEAM basal shear for pure zirconium, $\theta = 0$, compared to DFT curve

Chapter 4

Development of Binary Alloy 2nnMEAM potential

4.1 Creating the 2nnMEAM

In order to identify a more general approach to creating a new binary alloy 2nnMEAM potential, the whole process will be divided into four steps:

1. MEAM potential for pure elements
2. Pair interaction
3. Universal equation of state (UBER)
4. Determination of 2nnMEAM parameters

4.1.1 MEAM potential for pure elements

Pure element MEAM results for Zr and H will be used as the starting point for the creation of the new 2nnMEAM potential. The binary alloy 2nnMEAM potential is based on the MEAM potentials of the two composing pure elements. For hcp Zr data will be taken from Kim et al. [31] and for dimer H (dimer H is used to describe the hydrogen bond) from Lee [7]. It should be mentioned that Lee et al. modified the MEAM parameters for hydrogen by adding the $\beta^{(3)}$ parameter to the original hydrogen set from Dr.Baskes [3]. That parameter does not have any effect on the separate pure elements, but does play a role in creating alloy interaction between Zr and H.

	E_{coh}	r_e	B	A	$b^{(0)}$	$b^{(1)}$	$b^{(2)}$	$b^{(3)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$	C_{min}	C_{max}	d
H [7]	2.37	0.74	2.96	2.5	2.96	3.0	3.0	2.5	0.2	-0.1	0.0	2.0	2.8	0.0
Zr [31]	6.36	3.2	0.97	0.68	2.45	1.0	3.0	2.0	6.3	-3.3	-10.0	1.0	1.44	0.0

Table 4.1: MEAM potential parameters for the pure Zr and H

4.1.2 Pair interaction

As mentioned in the previous chapters, the same method that is used to determine pair interaction of the pure element atoms is used to determine pair interaction in an alloy system. A perfectly ordered intermetallic compound, with first neighbor atoms of the different type and second nearest neighbor atoms of the same type is used as a reference structure. In this case, diamond structure (B3-Zinkblende) is used to describe zirconium hydride.

4.1.3 Universal equation of state (UBER)

The parameters necessary to determine the equation of state for a given reference structure are: the cohesive energy E_{coh} , r_e the equilibrium first neighbor distance in the reference structure, the bulk modulus B and model parameter d . They can be assumed, determined by an experiment or obtained from first principles calculation. The model parameter d can be determined by fitting to the $\frac{\partial B}{\partial P}$ value of the reference structure. If the reference structure is not a real phase, it is difficult to estimate its value for alloys. In that case, d is usually assumed as the average of the pure element values [7].

In our case we can start with using bulk properties from the MEAM created by Baskes. The previous tests showed that MEAM was able to handle reasonably well the bulk properties like elastic constants and bulk modulus. Values calculated were similar or close to experimental values, so all UBER parameters, as well as the reference structure, can also be used for the new 2nnMEAM potential. What the MEAM was not able to reproduce are mainly the elastic constants of the ϵ and δ zirconium hydride, and it failed to maintain stability of all solid solutions during shear tests. So, the focus will be on the screening function parameters, modifying of the cut-off radius, the cohesive energy, as well as the MEAM library parameters provided with LAMMPS and investigating their influence on the physical properties, and especially on achieving agreement with the DFT shear tests.

4.1.4 Determination of the 2nnMEAM parameters

A total of 13 parameters need to be determined, 4 of which are from the equation of state (E_{coh} , r_e , B and d), 8 are C_{min} and C_{max} and the final one is the ρ_0 . As seen in Table 4.1, each pure element has its own C_{min} and C_{max} , because all interaction are between atoms of the same type (A-A-A or B-B-B). On the other hand, in alloys there are 4 different cases for screening (A-B-A, B-A-B, A-A-B, and A-B-B) that need to be taken into consideration. In this notation (A-B-C) means the screening effect of a B atom on a bond between A and C atoms.

The first step is to modify the 2nnMEAM library file in Table 4.2 and input parameters from the pure element MEAM for zirconium and hydrogen in Table 4.1. The values marked 'Old' are from Baskes' MEAM [36].

A fitting procedure is used to optimize all parameters so that certain physical properties, experimental or first-principles results could be replicated by the MEAM potential. Although, it is not always clear how certain factors influence some physical properties, with enough available data, MEAM potential can be created to replicate some, if not all, phases and transformations in the material. The main requirement is for a new interatomic potential to correctly reproduce as many equilibrium intermediate compounds and their physical properties [30]. Often, there are not enough data, so certain parameters are assumed or created from an average of the pure element MEAM data.

There are several paper dealing with creation of the binary 2nnMEAM potentials from the pure element MEAM potentials. As an example of a fitting procedure, the method of Lee et al. [7] will be used, with the main fitting parameters shown in the Table 4.3. All fitting parameters for the 2nnMEAM translated into LAMMPS are presented in Table 4.4.

Parameters with (i,j) mean all combinations of (i,j), for example $lattce(i,j)$ which describes the crystal lattice of the pure elements 1 and 2, $lattce(1,1)$ and $lattce(2,2)$, and that of their alloy $lattce(1,2)$. $C_{min}(i,j,k)$ means a minimum value of the screening factor where the interaction between atoms i and j starts to be fully screened by the atom k . On the other hand, $C_{max}(i,j,k)$, means the value where atom k does not interfere in the interaction between atoms i and j . Then those two atoms are unscreened by the atom k . In between those two extreme values atom k partially

MEAM library					
Parameter	Zirconium		Hydrogen		Description
	Old	New	Old	New	
elt	'ZrN'	'ZR'	'Hz'	'HH'	element
lat	'fcc'	'hcp'	'dim'	'dim'	lattice
z	12	12	1	1	# neighbors
ielement	40	40	1	1	atomic number
atwt	91.224	91.224	1.0079	1.0079	atomic weight
alpha	4.46	4.46	2.96	2.96	MEAM
$b^{(0)}$	4.2	2.45	2.96	2.96	MEAM
$b^{(1)}$	1.5	1	3	3	MEAM
$b^{(2)}$	5.7	3	3	3	MEAM
$b^{(3)}$	1	2	3	2.5	MEAM
alat	4.533	3.2	0.74	0.74	lattice constant
esub	6.325	6.36	2.235	2.37	$E_{coh}/atom$
asub	1.03	0.968	2.5	2.5	MEAM
$t^{(0)}$	1	1	1	1	MEAM
$t^{(1)}$	7	6.3	0.2	0.2	MEAM
$t^{(2)}$	4.5	-3.3	-0.1	-0.1	MEAM
$t^{(3)}$	-5.5	-10	0	0	MEAM
ρ_0	0.63	1	16	18	electron density
ibar	0	3	0	3	function G (see Eq.2.2.17,2.2.18,2.2.19)

Table 4.2: All MEAM library fitting parameters for the 2nnMEAM potential in LAMMPS [6]. The ibar parameter selects the form of the function G used to compute the electron density. MEAM in the description means that it is the standard MEAM parameter described in detail in [3].

screens their interaction, as described in section 2.2.6. In LAMMPS $C_{min}(1, 2, 1)$ and $C_{min}(2, 1, 1)$ are the same so only one needs to be declared. For example, $C_{min}(1, 2, 1)$ and $C_{min}(2, 1, 1)$ both describe the interaction between atoms of the type 1 and 2 being screened by the atom of the type 1 in between them.

Parameter	Selected value	Fitting procedure
E_{coh}	$0.5E_{coh}^{Fe} + 0.5E_c^H + 0.164$	Fitting dilute heat of solution of H in bcc and fcc Fe
r_e	1.835	Fitting lattice parameter of NaCl-type FeH and for better overall agreement
B	2.95	Fitting first-principles bulk modulus of NaCl-type FeH MEAM
d	$0.5d^{Fe} + 0.5d^H$	Assumption
$C_{min}(Fe - H - Fe)$	$0.36 = C_{min}^{Fe}$	Assumption
$C_{min}(H - Fe - H)$	$2.0 = C_{min}^H$	Assumption
$C_{min}(Fe - H - Fe)$	2.15	Relative size of heat of solution in bcc and fcc Fe
$C_{min}(Fe - Fe - H)$	$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^H)^{1/2}]^2$	Assumption
$C_{min}(Fe - H - H)$	$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^H)^{1/2}]^2$	Assumption
ρ_0	$\rho_0^H / \rho_0^{Fe} = 18$	For better overall agreement

Table 4.3: An example of a set of 2nnMEAM potential parameters for the binary Fe-H alloy system and fitting procedure, taken from [7]

4.1.5 Fitting methodology

The second nearest neighbor MEAM, 2nnMEAM, has to be fitted to simulate three stacking fault curves presented in Fig.3.5. All parameters from Table 4.4 are assumed constant, except the ones presented in the table 4.5. Those are the main fitting parameters used in this thesis: cut-off radius r_c which limits the area where interactions between atoms are calculated by the potential and screening function parameters $C_{min/max}(i, j, k)$. They were used to create many different 2nnMEAM potentials and test their ability to correctly simulate stacking fault results. Table 4.5 presents the final values used in 2nnMEAM.

In order to introduce some methodology to the trial and error approach of fitting, following assumptions have been made. Of the three DFT stacking fault curves in Fig.3.5 the most demanding in terms of fitting was the $\theta = 0.5$ due to the highest number of hydrogen atoms and biggest changes in excess energy observed during testing. That curve will be fitted first, followed by $\theta = 0.125$ and $\theta = 0$.

Then, three groups of 2nnMEAM potentials were made depending on the cut-off radius values. The first value was $r_c = 5.2$ from Kim et al. [31], followed by $r_c = 5$ and $r_c = 4.5$. Each of those three groups will have the same starting values for screening

parameters as described in Table 4.5. Now, $C_{min}(i, j, k)$ values were varied between assumed values of 0.8 and 2 and $C_{max}(i, j, k)$ between 1.44 and 3.

Whenever there is a good result for $\theta = 0.5$ 2nnMEAM the other two curves have to be tested with that potential. If they do not match the DFT results, $\theta = 0.5$ 2nnMEAM has to be fine tuned and again tested on the two remaining curves. If that does not fix the problem, a new $\theta = 0.5$ 2nnMEAM has to be found and the process repeated until there is a match between 2nnMEAM results and DFT results.

4.2 Testing New 2nnZrH MEAM

The first test, Fig.4.1, is the 2nnMEAM result for pure zirconium, $\theta = 0$, basal shear with and without relaxation. All results were presented on graphs where the y-axis presents the excess energy change per slip area, given in $[J/m^2]$, and the x-axis is the displacement along $1/3(01\bar{1}0)$ hcp direction. Both curves are smooth, apart for the small jumps around unstable stacking fault on the "no relax" curve. The starting configuration fully relaxes into perfect hcp lattice.

Figure 4.1: 2nnMEAM pure zirconium, $\theta = 0$, basal shear with and without relaxation. The left y-axis is for the fully relaxed curve, and the right y-axis for unrelaxed.

The same 2nnMEAM potential was used on all solid solution stacking fault tests, meaning for $\theta = 0.0625$, $\theta = 0.125$ and $\theta = 0.5$.

Similar results to that in Fig. 4.1 are obtained for 2nnMEAM handling of the $\theta = 0.0625$, Fig.4.2, $\theta = 0.125$, Fig.4.3, and $\theta = 0.5$, Fig.4.4. Unrelaxed curves are periodic and smooth, apart from $\theta = 0.5$ which has bigger changes in excess energy and excess energy values are negative. With each hydrogen atom added into the slip zone, excess energy is reduced overall, and ends up being negative in the case of the

$\theta = 0.5$. This means that with every hydrogen atom added, it is easier to slip the structure to that extent that for $\theta = 0.5$ the structure would collapse on its own into some more stable configuration.

Figure 4.2: 2nnMEAM pure zirconium, $\theta = 0.0625$, basal shear with and without relaxation. The left y-axis is for the fully relaxed curve, and the right y-axis for unrelaxed.

Figure 4.3: 2nnMEAM pure zirconium, $\theta = 0.125$, basal shear with and without relaxation. The left y-axis is for the fully relaxed curve, and the right y-axis for unrelaxed.

Figure 4.4: 2nnMEAM pure zirconium, $\theta = 0.5$, basal shear with and without relaxation. The left y-axis is for the fully relaxed curve, and the right y-axis for unrelaxed.

Figure 4.5: 2nnMEAM pure zirconium, $\theta = 0$, basal shear, compared to DFT result

Figure 4.6: 2nnMEAM pure zirconium, $\theta = 0.125$, basal shear, compared to DFT result

MEAM file				
Parameter	Old	New	Default	Description
r_c	4.5	5.2	4	cut-off rad.
delr	0.1	0.1	0.1	cut-off smooth.
augt1	0	0	0	augm. $t^{(1)}$
gsmooth_factor			only for ibar= 0 or 4	
ialloy	0	2	0	no averag. of t param.
mixture_ref	0	0	0	no mixture averag.
erose_form	0	2	0	UBER funct.
lattce(i,j)	'dia'	'dia'	-	lattice
zbl(i,j)	0	0	0	ZBL potential
nn2(1,1)	0	1	0	second neighbors
nn2(1,2)	0	1	0	second neighbors
nn2(2,2)	0	1	0	second neighbors
attrac(i,j)	0	0	0	UBER funct.
repuls(i,j)	0	0	0	UBER funct.
$E_{coh}(1,2)$	3.23	3.23	-	cohesive energy
$C_{min}(1,1,1)$	1.2	1	2	Screening func.
$C_{max}(1,1,1)$	2.8	1.44	2.8	Screening func.
$C_{min}(2,2,2)$	2	2	2	Screening func.
$C_{max}(2,2,2)$	2.8	2.8	2.8	Screening func.
$C_{min}(1,1,2)$	2	1	2	Screening func.
$C_{min}(2,1,1)$	2	2	2	Screening func.
$C_{min}(1,2,1)$	2	1.457	2	Screening func.
$C_{min}(1,2,2)$	2	1.457	2	Screening func.
$C_{max}(1,1,2)$	2.8	1.44	2.8	Screening func.
$C_{max}(2,1,1)$	2.8	2.8	2.8	Screening func.
$C_{max}(1,2,1)$	2.8	2.8	2.8	Screening func.
$C_{max}(1,2,2)$	2.8	2.8	2.8	Screening func.

Table 4.4: All MEAM file parameters for the new 2nnMEAM potential in LAMMPS [6]

Parameter	2nnMEAM
r_c	4.5
$C_{min}(1, 1, 2)$	1
$C_{min}(2, 2, 1)$	2
$C_{min}(1, 2, 1)$	1.457
$C_{min}(1, 2, 2)$	1.457
$C_{max}(1, 1, 2)$	1.44
$C_{max}(2, 2, 1)$	2.8
$C_{max}(1, 2, 1)$	2.8
$C_{max}(1, 2, 2)$	2.8

Table 4.5: The main fitting parameters final values used for 2nnMEAM

Figure 4.7: 2nnMEAM pure zirconium, $\theta = 0.5$, basal shear, compared to DFT result

Chapter 5

Discussion and Conclusions

5.1 The Original MEAM Potential

The original MEAM is based on the first nearest neighbor interactions coupled with a severe screening function [40]. During testing of the original MEAM it was noticed that the energy of a relaxed intrinsic stacking fault in silicon in the diamond-cubic structure is considerably higher than the first principles calculated value [22], and that MEAM leads to problems in the surface calculations (outward relaxation of the top layer of all three surfaces of Si and Ge, whereas first principles predicts contraction). The MEAM potential does not correctly predict the diamond cubic stacking fault structure, so longer-range interactions controlled by the screening function have to be considered [3]. Similarly, there is a problem with the energy levels in all of the tests performed by the MEAM and the 2nnMEAM. At the same time, there is not enough data on the zirconium and zirconium alloys empirical potentials or MEAM stacking fault tests.

When the MEAM was initially applied to hcp structures, it presented new challenges to the model. The close packed hexagonal (HCP) structure is stacked in ABABAB... sequence and its unit cell is not cubic, which means that in contrast to a cubic one it allows for less slippage and less ductility. One of the most important parameters of the HCP structure is the c/a ratio and in most materials it is not an ideal ratio. Since the MEAM is not able to handle non-ideal ratios, the way to go about it was to first implement the model to the ideal ratio, and then perform fitting of the parameters to the experimental values of properties.

Additionally, problems increase when vacuum is introduced in the simulation box, due to deformation of hcp basal plane during the slip, the presence of the hydrogen

atoms and their strong interaction with the zirconium atoms and most importantly due to the phase changes that occur during the slip.

The MEAM potential was tested in its original form, as received from Baskes. The main purpose for this was to test how the MEAM potential handles different zirconium phases and zirconium hydrogen solid solutions. It is not clear how to improve the transferability of the MEAM, because none of the tests were successful. By handling better basic structures or simpler zirconium hydrogen arrangements it would be easier to build on them and gradually investigate the ability to simulate more complex ones.

Our MEAM potential was created for zirconium on the fcc lattice, which is not the equilibrium structure at the room temperature according to the phase diagram. The assumption is that the MEAM was specifically created to test the fcc arrangement of different zirconium hydrides.

Due to complexity of the MEAM's handling of hexagonal structures mentioned above, it was obvious, that the MEAM based on the cubic structure of zirconium would further limit its ability to simulate shear response of zirconium hydrogen solid solution on the basal plane. The MEAM was not able to relax even the pure zirconium hcp in vacuum without deforming the stacking order of its layers. The layers A-B moved closer and created more cubic crystal zones, but at the same time those pairs separated farther apart from neighboring pairs.

By analyzing the behavior of structures during the shear tests, the main observation is their instability. Sequential slip relaxation was performed and after each slip the structure basically moved farther away from hexagonal and closer to the cubic arrangement of atoms. The MEAM has a strong screening function and its interactions are limited to first-neighbor ones. So, as soon as atoms in the shear zone separate from each other too far, there is no equilibrium of forces on them and they move away from the layer, and sometimes create small groups of cubically arranged atoms. Furthermore, when hydrogen is present, breaking of the symmetry is more evident. Longer range interactions are necessary to keep the structure stable and accommodate more intense many atom interactions, especially when hydrogen is present in the solution.

The zirconium hydrogen interaction is apparently more dominant than anticipated. The ease of movement of hydrogen within a crystal lattice, due to its small size, does not translate to higher ability to deform of the zirconium hydrogen solid

solution. It was noted that the excess slip energy goes down as the hydrogen concentration increases, thus enabling more ductile fracture, but at the same time the overall structure is less stable during shearing. The MEAM potential is not able to handle hydrogen addition to the already weak hcp crystal structure.

The tests with fully occupied tetragonal positions in the zirconium hydrogen solid solutions show that hydrogen increased the stability of the structure overall compared to the MEAM tests with pure zirconium as bulk. The hydrogen zirconium bond reduced the effect of longer distances between zirconium atoms in hcp than in fcc, for which the MEAM was developed. Zirconium d orbital electrons are supposed to form the covalent bonds with hydrogen atoms at the expense of weakening of the metallic bonding among zirconium atoms [4].

MEAM potential was not able to successfully perform any of the three DFT tests for zirconium hydrogen solid solution, so no direct comparison can be made between the two.

5.2 The New 2nnMEAM for Zirconium Hydrogen Solid Solutions

Fig.5.1 presents a direct comparison between DFT and 2nnMEAM results for the basal shear of zirconium hydrogen solid solutions. The pure zirconium lattice was slipped with different concentrations of hydrogen atoms in the slip zone. Our main point is the qualitative similarity between those two tests. All the tests have the peak in unstable stacking fault at the same level of slip as the DFT results, and change in a similar fashion before and after the peak. The 2nnMEAM was able to simulate the drop in excess energy with the increase in hydrogen concentration. There is also a quantitative similarity between the ratios of values of the unstable stacking fault energy on both diagrams, which range between 1.5-1.6 for the pure zirconium and $\theta = 0.125$, and 2.3-2.5 for pure zirconium and $\theta = 0.5$.

One of the characteristics of the MEAM formalism are its fitting parameters. They are based on the reference structure properties and fine-tuned according to the physical characteristics of the material, most commonly obtained from first principles. Each of the stacking fault tests can be viewed as a separate physical property because ideally 2nnMEAM requires special fine-tuning for each of them. Here, only one set of the parameters, one 2nnMEAM potential, was used successfully for all of them and

proved its ability to simulate stacking fault of different solid solutions.

Figure 5.1: DFT and 2nnMEAM zirconium hydrogen solid solution basal shear comparison

Stacking faults in the hcp basal plane consist of the original hcp structure and a strongly distorted local fcc structure that contains hydrogen atoms. Hydrogen atoms are more stable in the fcc lattice than in the hcp lattice [4], and a lowered unstable stacking fault with added hydrogen atoms present can be interpreted as the pure zirconium stacking fault reduced by hydrogen atom stability in the local fcc lattice. As slabs move relative to each other in the slip zone, local cubic arrangements of zirconium and hydrogen atoms form and therefore reduce the excess energy.

In the $\theta = 0.5$ test, only the full layer of hydrogen atoms was possible because of the interaction between zirconium and hydrogen atoms. If all hydrogen atoms are lined up in one layer, symmetry is retained in the arrangement of atoms and their bonds in the slip zone. On the other hand, random arrangement of hydrogen atoms in the slip zone was difficult to simulate due to very long computation time, breaking of hcp layers, loss of symmetry and equilibrium of forces/bonds between zirconium and hydrogen atoms.

5.3 Conclusion

This thesis was created with the goal of assembling a new 2nnMEAM potential for zirconium hydrogen solid solutions and demonstrating its ability to handle the complexities of the stacking fault tests fairly accurately. Baskes' MEAM potential for zirconium hydrides was used both as a basis for the creation of the 2nnMEAM and for comparison. 2nnMEAM is viewed as a potential tool for better understanding of the DHC phenomena, if only in a general way. The thesis consists of the short review of the zirconium hydrogen system, atomistic simulations, the MEAM formalism and testing, and development of the 2nnMEAM.

The main part is stacking fault tests of the $\theta = 0, 0.125, 0.5$ zirconium hydrogen solid solutions. Prior to them the MEAM potential was successfully used to calculate the basic properties of the variety of zirconium hydrides. But, MEAM failed in all stacking fault tests. On the other hand, 2nnMEAM was successful in all three tests and once again proved the advantages of the 2nnMEAM formalism.

The main challenge was finding the right fitting parameters for the new 2nnMEAM. Although, separate 2nnMEAM potentials might have been created for each of the three tests, our focus was more on the transferability of the new 2nnMEAM. DFT results were used for fine-tuning.

2nnMEAM is capable of simulating a realistic response of the solution during shearing. 2nnMEAM results were qualitatively very similar to DFT results, although energy levels were noticeably higher than in DFT tests. At the same time, the ratios of the unstable stacking faults of the pure hcp zirconium to $\theta = 0.125$, and the pure hcp zirconium to $\theta = 0.5$ were similar.

In order to improve the results of this thesis, better optimization has to be implemented and new calculations of the reference structure need to be done with first principles. Furthermore, more DFT results for stacking fault tests of zirconium hydrides would give a better insight of the zirconium hydrogen interaction and help create a better 2nnMEAM.

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Appendix A

Stacking Fault

An ideally symmetrical crystal would consist of atoms occupying all points on the three-dimensional perfect lattice. One can choose a different unit cell pattern or arrangement and infinitesimally repeat it in all directions to produce the perfect crystal. In nature, crystal structures incorporate many different imperfections. Some of them visible to the naked eye, some so tiny that only special equipment like electron microscopes enables us to visualize them. This range of macroscopic and microscopic imperfections we call crystal defects. Here we will focus only on the atomistic scale, because it is more relevant to this research.

Basic classification of defects [41], presented in the Fig.A.1, is as follows: point defects (e.g., vacant position on the lattice - vacancy or interstitial atom in between atoms - interstitial), line defect (dislocation line), planar defect (e.g., stacking fault and twin boundary), and volume defects (e.g., voids and gas bubbles). All attention will be on the planar defects in a crystal because all tests involve sliding motion between crystal blocks.

Planar defects range from large angle grain boundary, which has incoherent interface and subsequently high energy content per unit surface, to atomic planes in a crystal which have changed stacking of atomic layers compared to the stacking order of layers in the crystal. Those are twin interfaces and stacking faults, and they retain the coherency of the interface, which in turn carries lower energy content per unit surface.

Stacking faults are common in metals, particularly in fcc and hcp structures. Both fcc and hcp crystals are similar in the way the close packed layers of atoms are stacked to produce the crystal. Fcc (111) plane is the same as hcp basal (0001)

Figure A.1: Crystal defects: a) Interstitial and vacancy; b) Dislocation line; c) Planar defect - twin; d) Volume defect - void

plane, as depicted in Fig. A.2. What distinguishes fcc stacking from hcp stacking is the third layer, C, in the fcc, so fcc stacking sequence is ABCABCABC, whereas hcp's is ABABAB. Shifting or sliding of close-packed layers creates stacking faults or mis-stacking of layers. Three most common ones, presented in Fig. A.2, are: intrinsic, extrinsic and twin faults. Intrinsic fault is created by removing of one close packed layer, or shifting the top block of the crystal to the closest nearest neighbor position on the plane. Extrinsic fault is the opposite of the intrinsic, so one additional plane is added to the stacking order, whereas twin fault is an interface of the two crystals in a mirror-like arrangement relative to the slip plane.

Figure A.2: Planar view of the fcc (111) plane and Different stacking fault options:
a) perfect fcc crystal, b) intrinsic fault, c) extrinsic fault d) twin fault,
and e) twin crystal

Fig. A.3 depicts how a simple slip of the two layers, namely layers C and B, to positions of layers A and B respectively, creates fully coherent interface between fcc and hcp crystals. Example used presents martensitic transformation in steels. Any such rigid translation of the entire layer results in a stacking fault in the crystal and

is characterized by interface energy, stacking fault energy, γ_{sf} .

Figure A.3: FCC to HCP stacking transformation

Now, it is important to address strain energy change during stacking fault formation. Let's consider a perfect cubic lattice during shear. The top and bottom layer are sheared, and starting structure condition is defined by b which is the distance between closest neighbors in a layer and h which represents stacking height or the vertical distance between stacked layers, Fig.A.4. b is equal to the Burger ¹ vector of a full dislocation. Burger vector represents the magnitude and direction of the lattice distortion by dislocation in a crystal. Shear stress τ is a periodic function of the displacement δ . Before any shear stress is applied, $\Phi = \int \tau d\delta$ energy per unit area of the slip plane, is equal to zero. Point b) represents a homogeneous shear in the direction of the displacement. Point c) and d) are sheared pass the maximum shear stress value and are not homogeneous. Point d) represents the point of zero shear stress and displacement equal to one half of the Burger vector, b . This point is the unstable equilibrium state, and area under the stress displacement curve is the work needed to create it. That is the unstable stacking fault γ_{US} and it corresponds to the maximum value of Φ along the slip path, Fig.A.5.

¹named after Dutch physicist Jan Burgers

Figure A.4: Simple cubic lattice in a state of shear; position d) shows unstable stacking configuration with energy γ_{us} per unit area of slip plane

Important contribution of Rices theory [42] is that the value of γ_{us} can be obtained from theoretical calculations without any ambiguity. Let's consider a block like shear where an infinite crystal is cut in half along a plane, and the upper half is sheared with respect to the lower half by a displacement vector $\vec{f}$. As mentioned before, $\Phi(\vec{f})$ is the energy per unit area on the slip plane associated with this displacement. This energy surface, $\Phi(\vec{f})$, obtained as a function of the generalized displacement vector $\vec{f}$ is called the generalized stacking fault (GSF) energy surface or γ surface.

Figure A.5: Energy $\Phi = \int \tau d\delta$ associated with the slip displacement

Important alloying element for zirconium is hydrogen. Hydrogen significantly reduces stacking fault excess energies, and possibly contributes to enhanced planar slip and hindering cross-slip. That is in agreement with the predictions of the hydrogen enhanced localized plasticity (HELP) model [14]. Similar results are presented in [4, 43], where [4] is the basis for this research.

Appendix B

Delayed Hydride Cracking

Many transition metals, group V metals, create solid solution with hydrogen and that creates a problem because hydrogen reduces structural integrity of those metals. There is a wide range of examples of hydrogen related embrittlement, of which zirconium application in nuclear industry fuel cladding is one of the most experimentally investigated cases. Zirconium, like many other metals, forms hydrides when hydrogen penetrates its structure [44]. Metals can be exposed to hydrogen penetration either during manufacturing, forming or finishing, or during the final product application.

Among several proposed mechanisms by which hydrogen embrittles a material, researchers are currently focusing on three well-known categories [45]:

- delayed-hydride cracking (DHC),
- hydrogen-induced decohesion (HED),
- hydrogen-enhanced localized plasticity (HELP).

Delayed-hydride cracking (DHC) is characterized by new hydride phases that reduce the stress required for crack propagation. The focus of studies of DHC is on understanding of the role of hydrogen in the metal and the interaction between hydrogen and dislocation motion. Detailed analysis of DHC follows below.

Hydrogen-induced decohesion (HED) theory is focused on the reduction of the bond strength of the material near the crack tip because of the presence of hydrogen atoms. It is largely based on some observations of the cleavage with little local deformation, and supported by certain calculations. But, substantial experimental evidence has not been obtained to support the theory.

Hydrogen-enhanced localized plasticity (HELP) mechanism is based on the enhanced mobility of dislocations when hydrogen atoms are present in the solid solution. Mobility of dislocations is enhanced twofold, by increased speed of dislocation progression and lower applied stress is needed to move the dislocation.

The main parts of any nuclear reactor are the fuel, moderator and coolant. CANDU (CANadian Duterium Uranium) nuclear reactor uses natural uranium dioxide as fuel with heavy water serving as both moderator and coolant. Fig.B.1 depicts the main design feature of the CANDU reactor. Fuel pallets are placed in the fuel bundle, which goes into pressure tube. CANDU reactor vessel is called Calandria and has many fuel channels, each of which houses one pressure tube within an outer Calandria tube.

Figure B.1: CANDU fuel pallet, fuel bundle, pressure tube and Calandria

The fuel channel, Fig.B.2, presents one of the main features of the CANDU design. The main functional task of fuel channel is to locate the fuel in the reactor core and allow the pressurized Primary Heat transport (PHT) coolant to flow through it and efficiently remove the heat generated in the fuel by the nuclear fission process. Furthermore, they allow refueling while the reactor is operating at full power. Pressure tubes are about 6m long, with inside diameter of 104 mm, and 4 mm thick. Pressure tube is made of cold-worked zirconium alloy (Zircaloy). Zirconium alloys are used

in water reactors because of their low capture cross-section for thermal neutrons and good mechanical and corrosion properties. Calandria (reactor core) is a low-pressure tank that contains heavy water moderator. As depicted in Fig. B.2, fuel channel consist of pressure tube, which contains the fuel, placed in the calandria tube. On both ends, there are feeders for circulation of the coolant.

Figure B.2: CANDU fuel channel

Pressure tube with fuel bundle is placed in calandria tube to form fuel channel. In order to create tight seal between pressure tube and calandria tube, mechanical joint is created. Tube end is placed inside a thick-walled tube of 403 stainless steel with three internal, circumferential grooves, Fig.B.3. The pressure tube is internally rolled to make a seal at the grooves, and thus create a so-called rolled joint. If the tube is rolled too far part of the pressure tube is deformed without support which results in high tensile stresses. If a crack penetrates the tube wall, coolant water leaks and is detected, and the reactor is shutdown. The cracks initiated on the inside surface grew by DHC radially and axially in a series of crack growth bands [46]. The cracks grew at room temperatures by DHC, but at operating temperature of the reactor all hydrogen is in the solution and cracking stopped. So each band represents shutdown

of the reactor and period of operation. In order to prevent further occurrences of DHC the residual stresses were minimized by stress-relief or redesign of the rolled-joint.

Figure B.3: Rolled joint between fuel channel and end fittings

One of the most crucial findings of the DHC analysis is the one about orientation of the hydride platelets in the pressure tube wall. Radial hydride platelets with normal parallel to circumferential normal and tensile stress, extremely reduce tensile ductility at room temperature, Fig.B.4.

Figure B.4: Hydride platelets orientation in the pressure tube wall

The process of DHC embrittlement itself takes two forms. The first one is the short term loss of toughness, and second is a stable, time-dependent crack growth mechanism called delayed hydride cracking (DHC). For DHC to occur, besides hydrogen presence in the structure of the metal, it needs a "stress-raiser", such as a crack, and a source of tension. Such tensile stress can be produced internally by residual stresses, or imposed externally, by a work load [9].

DHC, or the first step of DHC, requires three basic steps, as presented in the Fig. B.5:

- a) The nucleation of hydrides at the "stress-raiser". Zirconium hydride platelets are oriented circumferentially near the "stress-raiser"
- b) Hydride growth and orientation. Due to tensile stress and "stress-raiser" hydride platelets orient themselves radially and at the tip of the "stress-raiser"
- c) When all the requirements are fulfilled, e.g. hydrogen concentration, hydride platelet size and tensile stress, hydride cracks and crack extends deeper from the surface into material.

Figure B.5: Single step in DHC process

Hydrogen is present in the bulk of the material and it diffuses towards the crack tip area due to the gradient of the chemical potential [46, 47]. Both the stress state

and concentration of hydrogen in the material determine the chemical gradient. That gradient is the main driving force for movement of hydrogen in solution to the crack tip.