Molecular Dynamics Simulation of Zirconium and Zirconium Hydride

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Abstract

Molecular dynamics simulations were performed on pure α-Zr and δ-ZrH_2 in order to obtain a proper choice of potential. The EAM and MEAM potential were able to successfully predict the variation in Lattice parameter and Elastic Modulus with the experimental results. Interfacial cracking of zirconium hydride was observed with use of MEAM potential. A proper choice of potential paves a way for studying complicated engineering problems like failure due to hydride reorienting in zirconium.

1. Introduction

Zirconium a Group IV Transition metal is very important in design of cladding devices in Nuclear Reactors [1]. It has a very low absorption of neutrons .The crystal structure of pure zirconium (α-Zr) is hexagonal packed structure (HCP) at room temperature. Zirconium exhibits interesting properties such as temperature dependent phase change and deformation under stress caused due to twinning [2]. Zirconium with atomic number 40 and atomic mass of 91.224 and hydrogen with Atomic number 1 and atomic mass of 1.007 react to form the zirconium hydrides (δ-ZrH_2) at 800°C .The hydride formation is the source of interest as it is responsible for cracking in metals. The δ-ZrH2 formed is a face centered Cubic (FCC) structure consists of hydrogen occupying the tetrahedral sites (T-sites). The Interface of α-Zr and δ-ZrH_2 has been source of interest. The change in orientation of these hydrides due to application of stress is responsible for cracking in nuclear fuel rods [3].This has also been proved through the thermodynamic modeling [4].

However, the behavior of the interface of α-Zr and δ-ZrH2 at atomic level has not been studied .The behavior of hydrogen through computer simulated Molecular Dynamics requires good understanding of crystal structure and potentials which calculates the forces with which the atoms interact with each other [2]. The best approach for determination of forces is EAM (Embedded Atom Method) proposed by Daw and Baskes as it was suggested that Finnis and Sinclair (FS) potential is not accurate as predicted by Marchese, Jacucci, and Flynn[5].

2. Embedded Atom Method (EAM)

EAM (Daw and Baskes 1983) is a semi-empirical method which calculates random arrangement of positions of the atoms in pure metals and alloys. The total energy of the system is evaluated by two factors one is the interaction of every atom with local electron density with the entire system of

atoms called embedding energy and second is pairwise interactions creating electrostatic interactions between atoms. It can be written in the form of equation [5].

$$E_{tot}=\Sigma F_i(\rho_i) + \tfrac{1}{2}\sum_{i\neq j} \emptyset_{ij}(R_{ij}) \quad (1)$$

The expression F_i is the embedded energy of atom i, (ρ_i) is the electron density of atom i, $\emptyset_{ij}(R_{ij})$ gives the pair interactions between atom i and j with a distance(R_{ij}).The electron density of each site is computed using electron density which is given by the equation.

$$(\rho_l)=\sum_{j\neq i} (\rho_j^a)(R_{ij}) \quad (2)$$

ρ_j^a R is atomic electron density at a distance R from the nucleus of the atom j. An empirical calculations are made for the pair interactions and embedded energies to fit sublimation energy, lattice constant, elastic constants, vacancy formation energy, and the zero temperature equation of state of the pure metals.

2.1 **Modified Embedded Atom Method (MEAM)**

This method computes pairwise interactions for various materials using meam potential It is developed by Baskes[]. It is an extension of Embedded Atom Method (EAM).It adds angular forces it is suitable for different kinds of metals crystal structures such as FCC, HCP, diamond and also covalently bonded atoms. The total energy given is

$$E_{tot}=\Sigma \{F_i(\rho_i) + \tfrac{1}{2}\sum_{i\neq j} \emptyset_{ij}(R_{ij})\} \quad (1)$$

3. **Structure of Zirconium (α-Zr)**

4.

The electronic structure of zirconium is created with the lattice parameters from R.W.G Wyckoff at 300°K as shown in figure 4. EAM potential for Zr is used to evaluate change in lattice parameters as a function of temperature taken at minimum energy states. Periodic boundary conditions are used to avoid free surfaces. The electronic structure is evaluated for 900 atoms of single crystal of zirconium. The change in Lattice parameters are evaluated at constant temperatures by relaxing the structure. Figure 4 shows the arrangement of atoms in zirconium.

5. **Results and Discussion:**

4.1. Change in Lattice Parameters vs. Temperature using EAM Potential

There is increase in Lattice parameters with increase in temperature is observed. The values are in accordance with the Literature [6].This shows that the potential used for the structure is good.

Table I. Calculate Lattice parameters of ‘a’ and ‘c’ and comparison with the Experimental values

Temperature (°K)	'a'(Å) EAM	‘c'(Å) EAM	Experimental a[6] (Å)	Experimental c[6] (Å)
100	3.2365	5.1542	3.2294	5.14143
300	3.2375	5.1588	3.23312	5.14905
500	3.2418	5.1625	3.23641	5.15752
800	3.2527	5.18	3.24146	5.1737
1125	3.2689	5.2058	3.24479	5.19637

4.2 Stiffness Coefficients for α-Zr Using EAM Potential at 0K

Table II. Calculated elastic coefficients α-Zr for structure

Cij	1	2	3	4	5	6
1	141.52	74.27	74.08	0.00	0.00	0.00
2	74.27	141.52	74.27	0.00	0.00	0.00
3			167.72	0.00	0.00	0.00
4				43.93	0.00	0.00
5					43.93	0.00
6						33.63

The values of Lattice parameters and stiffness values are in good comparison with Literature [2].

Table III. Calculated parameters from stiffness matrix

Bulk Modulus(GPa)	Young's Modulus[100](GPa)	Poisson ratio
96.67	90.38GPa	0.34

4.3. Stress and Strain values for α-Zr Using EAM potential

The variation of stress and strain at various temperatures is shown in Figure 2. The Drop in stress is observed due to deformation of material. The variation stress and strain for different directions is shown in Figure 3

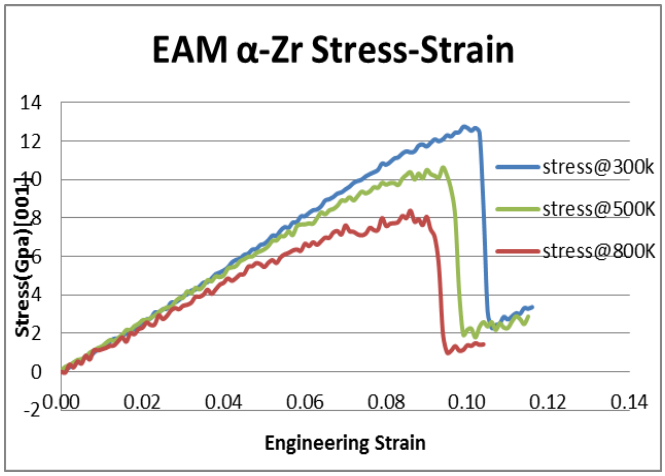

Figure 2

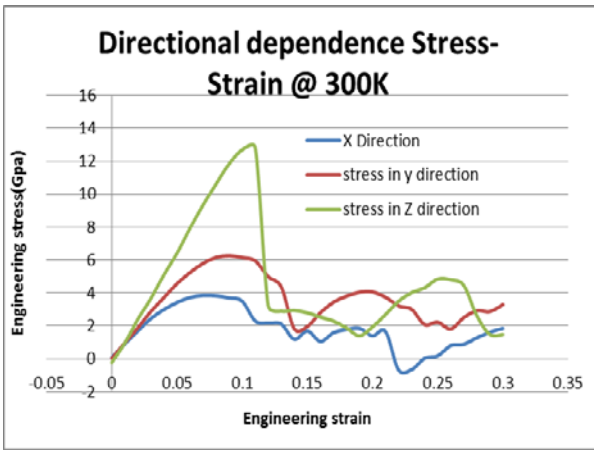

Figure 3

4.4. Zirconium Hydride(ZrH_2)

Initially zirconium hydride is created as a tetragonal structure with hydrogen atoms at tetrahedral sites. MEAM potential is used for this structure. Upon minimization it converts to FCC (δ-ZrH_2) which shows the tetragonal phase for this structure is unstable. The elastic values for δ-ZrH_2 are shown in Table III. Figure 5 shows arrangement of zirconium (Zr) and hydrogen (H)

Table III:-The stiffness values for δ-ZrH_2

Cij(Gpa)	1	2	3	4	5	6
1	209.91	89.84	89.84	0.00	0.00	0.00
2		209.91	89.84	0.00	0.00	0.00
3			209.91	0.00	0.00	0.00
4				20.41	0.00	0.00
5					20.41	0.00
6						20.41

Table IV:-Parameters calculated from stiffness matrix

Cohesive Energy(Ec) eV/atom	Lattice parameter(A°)	Bulk Modulus(GPa)	Youngs Modulus(GPa)	Poission Ratio
4.18	4.83	130	156	0.3

The stiffness values and Bulk modulus are in good comparison with the *ab inito* calculations of Literature [14]

4.5. Interfacial Fracture of Zirconium Hydride

Interface of zirconium has been interesting to many of the researchers. This work discusses the effect of stress on Interface between zirconium and zirconium hydride using molecular dynamics

using MEAM potential. An Interface of α-Zr- δ-ZrH_2- α-Zr is modeled. There are two different types of interface .One containing hydrogen at the Interfacial boundary and second is zirconium at the boundary. The structure is first equilibrated at 300K and stress is applied along X-direction. The figure 7 shows cracking of δ-ZrH_2 and interface due presence of hydrogen.

6. Conclusion:-

Molecular dynamics simulations using EAM potential are able to correctly predict the increase in lattice parameters increase in temperature for α-Zr. Also the stiffness values for α-Zr and δ-ZrH_2 are in good comparison with literature. A good match of the simulations with the existing experimental values validates the choice of potential used in the simulations. The fracture of δ-ZrH_2 is observed. The further analysis is to be done on reorientation of hydride on stress.

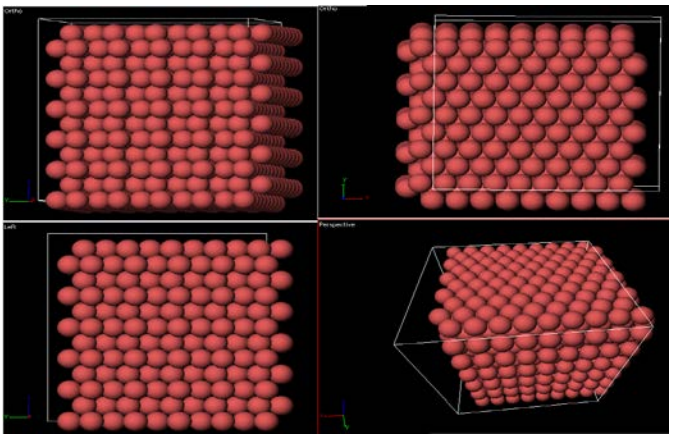

Figure 4 Shows α-Zr at different views

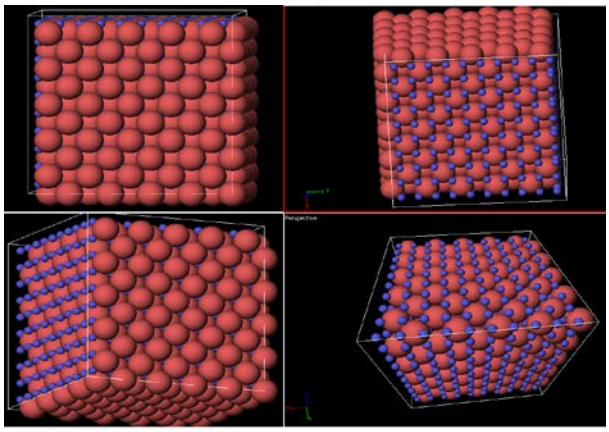

Figure 5 Shows δ-ZrH_2 (Red-Zr, Blue H)

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References:-

[1] Yan- Jun Hao , Lin Zhang , Xiang-Rong Chen , Ying-Hua Li and Hong-Liang He, “Phase transition and elastic constants of zirconium from first-principles calculations”, Journal of Physics, Condensed Matter**,** J. Phys.: Condens. Matter 20 (2008) 235230 (5pp).
[2] M. I. Mendelev and G. J. Ackland, “Development of an interatomic potential for the simulation of phase transformations in zirconium”, Philosophical Magazine Letters, Vol. 87, No. 5, May 2007, 349–359.

[3] N.A.P. Kiran Kumar[a] ,Jerzy. A. Szpunar[a], Zhang He[b], "Microstructural studies and crystallographic orientation of different zones and δ-hydrides in resistance welded Zircaloy-4 sheets", Journal of Nuclear Materials, Volume 414, Issue 3, 31 July 2011, Pages 341–351.
[4] W. Qin[a,], N.A.P. Kiran Kumar[b], J.A. Szpunar[a], J. Kozinski[a, c], "Intergranular δ-hydride nucleation and orientation in Zirconium Alloys", Acta Materialia, Volume 59, Issue 18, October 2011, Pages 7010–7021.
[5] Stephen M. Foiles and Murray S. Daw, "Calculation of the thermal expansion of metals using the embedded-atom method" Physical Review B , Volume 38, Number 17, 15 December 1988-I.
[6] J. Goldak, L. T. Lloyd, C. S. Barrett, "Lattice Parameters, Thermal Expansions, and Grüneisen Coefficients of Zirconium, 4.2 to 1130°K" , Physical Review, Volume 144, Number 2 1s April 1966.
[7] C. Domain[a,], R. Besson[b], A. Legris[b] "Atomic-scale Ab-initio study of the Zr-H system: I. Bulk properties " Acta Materialia, Volume 50, Issue 13, 1 August 2002, Pages 3513–3526.
[8] C.Korn, "NMR study comparing the Electronic structures of ZrH_x and TiH_x", Physical Review B Volume 28, Number 1, 1 July 1983
[9] E. S. Fisher and C. J. Renkea, "Single-Crystal Elastic Moduli and the hcp→bcc Transformation in Ti, Zr, and Hf", Physical Review, Volume 135, Number 2A, 20 JUL Y 1964,
[10]Stukowski, "Visualization and analysis of atomistic simulation data with OVITO - the Open Visualization Tool", Modeling Simul. Mater. Sci. Eng. 18 (2010) 015012, http://ovito.org/
[11] S. Plimpton, "Fast Parallel Algorithms for Short-Range Molecular Dynamics", J Comp Phys, 117, 1-19 (1995), http://lammps.sandia.gov.
[12] R. Zugic, B Szpunar , D. Krstic and U. Erb, "Effect Of Porosity On The Elastic Response Of Brittle Materials: an Embedded-Atom Method Approach" , Philosophical Magazine A, 1997, VOL.75, No. 4, 1041-1055.
[13] N.A.P. Kiran Kumar[a] ,Jerzy. A. Szpunar[a], Zhang He[b], "Preferential precipitation of hydrides in textured zircaloy-4 sheets", Journal of Nuclear Materials, Volume 403, Issues 1–3, August 2010, Pages 101–107.
[14] Szpunar .B , Baskes M.I. and Jochym P.T, "OXYGEN AND HYDROGEN DIFFUSION IN ZIRCONIA", 8th Int. Conf. on CANDU fuel, Delawana Inn, Honey Harbour, Ontario,(2003 September 21-24), Conference Proceedings
[15] M. I. Baskes, "Modified embedded-atom potentials for cubic materials and impurities", PHYSICAL REVIEW B VOLUME 46, NUMBER 5, 1 AUGUST 1992-I