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Abstract. Use of uranium–silicide (U-Si) in place of uranium dioxide (UO_2) is one of the promising concepts being proposed to increase the accident tolerance of nuclear fuels. This is due to a higher thermal conductivity than UO_2 that results in lower centerline temperatures. U-Si also has a higher fissile density, which may enable some new cladding concepts that would otherwise require increased enrichment limits to compensate for their neutronic penalty. However, many critical material properties for U-Si have not been determined experimentally.

It is anticipated that modeling and simulation may deliver guidance on the importance of various properties and help prioritize experimental work. In order to develop knowledge-based models for use at the engineering scale with a minimum of empirical parameters and increase the predictive capabilities of the developed model, inputs from atomistic simulations are essential. First-principles based density functional theory (DFT) electronic structure calculations may provide the most reliable information. However, it is probably not possible to obtain kinetic information such as amorphization under irradiation directly from DFT simulations due to size and time limitations. Thus, a more feasible way may be to employ molecular dynamics (MD) simulation. Unfortunately, so far no MD potential is available for U-Si to discover the underlying mechanisms.

Here, we present our recent progress in developing a U-Si potential. The development is based on the Tersoff type potentials for single element U and Si. The Si potential is taken from the literature and a Tersoff type U potential is developed in this project. With the primary focus on the U_3Si_2 phase, some other U-Si systems such as U_3Si are also included as a test of the transferability of the potentials for binary U-Si phases. Based on the potentials for unary U and Si, two sets of parameters for the binary U-Si system are developed using the Tersoff mixing rules and the cross-term fitting, respectively. The cross-term potential is found to give better results on the enthalpy of formation, lattice constants and elastic constants than those produced by the Tersoff mixing potential, with the reference data taken from either experiments or DFT calculations. In particular, the results on the formation enthalpy and lattice constants for the U_3Si_2 phase and lattice constants for the high temperature U_3Si (h-U_3Si) phase generated by the cross-term potential agree well with experimental data. Reasonable agreements are also reached on the elastic constants of U_3Si_2, on the formation enthalpy for the low temperature U_3Si (m-U_3Si) and h-U_3Si phases, and on the lattice constants of m-U_3Si phase. All these phases are predicted to be mechanically stable. The unary U potential is also tested for three metallic U phases (α, β, γ). The potential is found capable to predict the cohesive energies well against experimental data for all three phases. It matches reasonably with previous experiments on the lattice constants and elastic constants of αU.

Keywords: accident tolerant fuels; uranium–silicide (U-Si); multiscale modeling; density functional theory; molecular dynamics potential.

1. INTRODUCTION

The usage of triuranium–disilicide (U_3Si_2) in place of uranium dioxide (UO_2) is one of the promising concepts proposed to increase the accident tolerance of nuclear fuels in light water reactors [1]. U_3Si_2 has higher thermal conductivities than that of UO_2 at operating temperatures, resulting in lower fuel centerline temperatures. It also has a higher U density, which may enable some new cladding concepts that would otherwise require increased enrichment limits to compensate for their neutronic penalty. However, many materials properties of U_3Si_2 have not been determined and are required to have a good assessment of the in-reactor behavior of U_3Si_2. To mitigate the difficulties in getting all necessary data from experiments, electronic structure calculations such as density-functional-theory (DFT) calculations or atomistic molecular dynamics (MD) simulations can be utilized and are expected to generate needed data with better efficiency and reduced cost.

While parameter free DFT calculations are believed to be able to provide the most reliable information, it is probably not possible to obtain kinetic information such as amorphization under irradiation directly from DFT simulations due to size and time limitations. Thus, a more feasible way may be to employ molecular dynamics (MD) simulation. Unfortunately, so far no MD potential is available for U-Si to discover the underlying mechanisms. In the following, the development of a Tersoff type U-Si potential is described. We start with the introduction of potential fitting procedure in Section 2 and proceed with the potential parameters and fitting results in Section 3. A summary is given in Section 4.

2. POTENTIAL FITTING PROCEDURE

2.1 Potential Formalism and Fitting Scheme

To fit an interatomic potential, a formalism needs to be decided considering the bonding nature in the material system and the material properties of interest. For instance, in freshly fabricated U_3Si_2 fuels there are usually secondary phases such as U_3Si and/or USi [2]. Furthermore, silicide compounds (U_3Si_2 and U_3Si) are known to become amorphous under irradiation at low temperatures [2-4]. Based on the above considerations, the Tersoff type bond-order formalism [5, 6] is selected as it can treat both metallic and covalent bonding [7]. A Tersoff type Si potential existing in the literature has been shown to describe liquid and amorphous Si phases well, as well as other crystallographic phases of Si [8, 9]. Therefore, this Si potential is used here to describe the Si-Si interaction in U-Si systems. However, so far there have been no Tersoff type U potentials that can describe all possible U phases, α, β, and γ. To come up with a U-Si potential, we start with the development of a Tersoff type U potential. Based on the existing Si and the U potential developed here, cross-term parameters for U-Si interactions are fitted for binary U-Si phases including U_3Si_2 and U_3Si. During the fitting, we focus on the U_3Si_2 phase, which is the primary fuel candidate of our accident tolerant fuel high-impact-problem (ATF-HIP) project.

In MD simulations it is desired to capture both the thermodynamic and the kinetic properties. This sets a high standard for the interatomic potentials used in the simulations, for instance potentials that are fit by force matching with input data such as lattice, energy and force directly from first-principles DFT calculations. The software POTFIT [10] is suitable for potential fitting using force matching, and it was initially utilized here. Though using POTFIT to develop the potential is very promising, the fidelity of the fitted potential crucially depends on the reliability of the forces from DFT calculations. However, it was observed that in our DFT calculations γ-U experienced a BCC to BCT transition, leading to suspicion that the forces from the standard DFT calculations may have contributed to destabilize γ-U. It is further evident from the unexpected low specific heat capacity, C_v, of γ-U predicted by the DFT calculations that the forces calculated by DFT could be erroneous. This error was likely due to the limitation of traditional DFT method to handle the 5f-orbitals of metal U, which combines strong electron correlation, multi-minima, relativistic effects of 5f-orbitals and 5f electron delocalization/hybridization. Thus it is determined not viable to fit the U-Si potential using the force matching potential fitting package POTFIT.

Without taking force information into the collective dataset, the software GULP [11, 12] is used to fit the binary U-Si potential. GULP directly fits materials properties such as lattice parameters, total potential energies (based on cohesive or formation energies) and elastic constants of targeting crystal structures or phases. Note that GULP is not a force matching potential fitting package, in contrast to POTFIT. During fitting, we take the data from previous experiments [13, 14] and a recent DFT calculation [15] as reference.

Here the primary goal is to develop a binary U-Si potential for the U_3Si_2 phase. As a good Tersoff type U potential does not exist, we start with the fitting of the U interatomic potential. While focusing on the U_3Si_2 phase, we also try to pursue the transferability so that the potential can be used to study secondary phases, such as (α, β, γ)-U and U_3Si, which are one of the most important factors leading to the breakaway swelling in the performance of U_3Si_2 [2].

2.2 Tersoff Potential

In the Tersoff formalism [5, 6], the total potential energy of a material system, E, is defined as the summation of pair interactions V_{ij}:

$$E = \frac{1}{2}\sum_{j\neq i} V_{ij} \tag{1}$$

with V_{ij} given by the following equations:

$$V_{ij} = f_C(r_{ij})\left[f_R(r_{ij}) + b_{ij} f_A(r_{ij})\right] \tag{2}$$

$$f_C(r) = \begin{cases} 1 \quad : \quad r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi}{2}\frac{r-R}{D}\right) : R - D < r < R + D \\ 0 \qquad : r > R + D \end{cases} \tag{3}$$

$$f_R(r) = Ae^{(-\lambda_1 r)} \tag{4}$$

$$f_A(r) = -Be^{(-\lambda_2 r)} \tag{5}$$

$$b_{ij} = \left(1 + \beta^n \zeta_{ij}^n\right)^{-\frac{1}{2n}} \tag{6}$$

$$\zeta_{ij} = \sum_{k\neq i,j} f_C(r_{ik})\, g(\theta_{ijk})\, e^{\left[\lambda_3^m (r_{ij}-r_{ik})^m\right]} \tag{7}$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{\left[d^2 + (h - \cos\theta)^2\right]} \tag{8}$$

Here, r_{ij} is the distance between atoms i and j; f_A and f_R are the attractive three-body interactions and repulsive pair term, respectively; and f_C is a smooth cutoff function. The term ζ_{ij} defines the effective coordination number of atom i, i.e., the effective number of nearest neighbors, in which the relative distance of two neighbors r_{ij}-r_{ik} and the bond-angle θ are taken into account. With a minimum at $h = \cos\theta$ in the function $g(\theta)$, the parameter d determines the curvature or sharpness, and c expresses the strength of the angular effect. The summations in the formula are over all neighbors j and k of atom i within the cutoff distance R + D.

To fit a unary U potential, the lattice constants and cohesive energies of all three U phases are included in the fitting. The elastic constants of αU are also used in the fitting. The thus obtained parameters for U-U interaction are listed in Table 1.

Based on the existing unary Si potential [6] and the unary U interatomic potential developed here, the interaction between U atoms and Si atoms can be obtained in two ways. The first is to fit all the cross-term parameters using the experimental and/or DFT data. The thus obtained potential is referred to as the cross-term potential. The second is to calculate these parameters using the Tersoff mixing rule [5], with the resulting potential being the Tersoff mixing potential. The parameters for U-Si terms using the cross-term fitting are listed in Table I. For Tersoff mixing potential, the following U-Si parameters are needed:

$$\lambda_1^{Si,U} = \frac{1}{2}\left(\lambda_1^{Si} + \lambda_1^{U}\right) \tag{9}$$

$$\lambda_2^{Si,U} = \frac{1}{2}\left(\lambda_2^{Si} + \lambda_2^{U}\right) \tag{10}$$

$$A_{Si,U} = \chi_1 (A_{Si} A_U)^{1/2} \tag{11}$$

$$B_{Si,U} = \chi_2 (B_{Si} B_U)^{1/2} \tag{12}$$

$$L = (L_{Si} L_U)^{1/2} \tag{13}$$

$$S = (S_{Si} S_U)^{1/2} \tag{14}$$

where L=R+D and S=R-D. χ_1 and χ_2 are parameters for the fine adjustment of the simple interpolation to describe the strength of the heteropolar bond between U atom and Si atom. They are the only two parameters (χ_1 and χ_2) to be fitted and their values are 1.1366 and 0.8056, respectively. Furthermore, $\beta_{U-Si} = \beta_{U-Si} = 0$.

Table 1. Parameters for uranium, silicon, and the cross term of U-Si. R and D are not systematically optimized and m is fixed to 3. The Si parameters are taken from literature [6]. $\beta_{Si-U} = 0$.

	Si	U	U-Si (Si-U)
A (eV)	1830.8	540.8202	556.45915
B (eV)	471.18	179.4814	178.8864
λ_1 (Å^{-1})	2.4799	1.8333	1.82328
λ_2 (Å^{-1})	1.7322	1.1989	1.26005
β	0.0000010999	0.0000010999	0.000001 (0)
m	3	3	3
n	0.78734	0.78812	2.27619
c	100390.0	95575.5	148153.
d	16.218	16.15206	29.6570
h	-0.59826	-0.7168	-2.98962
λ_3 (Å^{-1})	1.7322	1.742313	1.64540
R (Å)	2.85	3.425	3.425
D (Å)	0.15	0.225	0.225

3. ASSESSMENT OF FITTING RESULTS

3.1 Results for the Tersoff Mixing Potential

3.1.1 U_3Si_2 Phase

The U_3Si_2 phase is the primary focus in this study. Table II lists the calculated material properties of the U_3Si_2 phase using the Tersoff mixing potential, compared with the data from either experiments such as the lattice constants (Å) [13] and the potential energy (eV) (derived from the formation energy from Ref. [14]) or DFT calculations of the elastic constants (GPa) [15].

The lattice constants of *a*, *b*, and *c* from the Tersoff mixing potential are 7.124 Å, 7.124 Å, and 3.789 Å, respectively. These results agree well with the experimental data [13] with the fitting errors below 3%. More specifically, the errors for the lattice constants of *a*, *b*, and *c* are -2.9%, -2.9%, and -2.37%, respectively. The crystal structure of U_3Si_2 is tetragonal with the space group P4/mbm (127) [13], in which the lattice constants of *a* and *b* should be equal. However, such criteria may not be always satisfied after the structure is full relaxed without symmetry constraints. In the fitting, *a* and *b* are allowed to change independently to avoid the appearance of metastable phases. For this reason, both *a* and *b* are listed in the table for the comparison with experimental data.

With the targeting potential energy of -52.53 eV for U_3Si_2 (10 atoms per unit cell), the calculated total potential energy is -55.939 eV. The corresponding error is ~6.5%. The corresponding enthalpy of reaction is predicted to be exothermic, which is consistent with the experimental observations in Ref. [14].

As listed in Table II, all elastic constants are significantly over predicted in reference to DFT results. An attempt to improve the elastic constants for the U_3Si_2 phase leads to further deviations of the predicted energy and lattice constants from the DFT results.

3.1.2 U_3Si Phase

There are two phases for U_3Si: m-U_3Si (space group I4/mcm (140) and 16 atoms per unit cell) at low temperature and h-U_3Si (space group Pm3m (221) and 4 atoms per unit cell) at high temperature [13]. As listed in Table II, the lattice constants given by the Tersoff mixing potential agree well with experimental data [13] for both phases of U_3Si. Specially, the lattice constant for h-U_3Si is 4.164 Å, corresponding to an error of about 4.19%. The cubic structure is maintained after being fully relaxed. The lattice constants *a*, *b*, and *c* for m-U_3Si are 5.89 Å, 5.89 Å, and 8.329 Å, respectively. The tetragonal structure is kept and the discrepancies for the lattice constants of *a*, *b*, and *c* from the experiments are -2.31%, -2.31% and -4.22%, respectively.

The total potential energies from the prediction and experiment for m-U_3Si are -98.118 eV and -86.15 eV, respectively, with an error ~13.89%. The corresponding enthalpy of reaction is predicted to be exothermic, which is consistent with the experimental observation in Ref. [14].

The elastic constants are not tested for both U_3Si phases. In an attempt to further reduce the error in the potential energies of h-U_3Si_2 and m-U_3Si, the discrepancies of the predicted elastic constants for U_3Si_2 with respect to the DFT results are found to increase.

In summary, the lattice constants and formation enthalpy for the U_3Si_2 phase and two U_3Si phases predicted by the Tersoff mixing potential are in good agreement with the experimental data. However, the elastic constants for U_3Si_2 are significantly over estimated.

Table II. Calculated material properties of U_3Si_2 and U_3Si phases using the Tersoff mixing rules, compared with the dataset from either experiment such as the lattice constants (a, b, c, in Å) [13] and cohesive energy E (eV) [14] or DFT calculations of the elastic constants C_{ij} (GPa) [15].

Atoms/UC	Phase	Type	Exp./DFT	Ca.	Error (%)
10	U_3Si_2	C_{11}	167.26	771.662	361.35
10	U_3Si_2	C_{33}	205.31	525.819	156.11
10	U_3Si_2	C_{12}	45.63	217.364	376.36
10	U_3Si_2	C_{13}	50.34	355.676	606.55
10	U_3Si_2	C_{44}	67.49	502.568	644.66
10	U_3Si_2	C_{66}	74.09	454.232	513.08
10	U_3Si_2	E	-52.53	-55.939	6.49
10	U_3Si_2	a	7.3364	7.124	-2.90
10	U_3Si_2	b	7.3364	7.124	-2.90
10	U_3Si_2	c	3.89	3.798	-2.37
4	h-U_3Si	E	-20.51	-24.529	19.60
4	h-U_3Si	a	4.346	4.164	-4.19
4	h-U_3Si	b	4.346	4.164	-4.19
4	h-U_3Si	c	4.346	4.164	-4.19
16	m-U_3Si	E	-86.15	-98.118	13.89
16	m-U_3Si	a	6.029	5.89	-2.31
16	m-U_3Si	b	6.029	5.89	-2.31
16	m-U_3Si	c	8.696	8.329	-4.22

3.2 Results for the Cross-term Potential

3.2.1 U_3Si_2 Phase

Table III lists the calculated material properties of the U_3Si_2 and U_3Si phases using the parameters listed in Table I, compared with the data from either experiment such as the lattice constants (Å) [13] and the total potential energy (eV) [14] or DFT calculations of the elastic constants (GPa) [15].

The lattice constants of *a*, *b*, and *c* for U_3Si_2 from the developed potential are 7.298 Å, 7.298 Å, and 3.899 Å, respectively. The agreement between the potential prediction and the experimental data [13] is excellent, with the errors being less than 1%. Specially, the errors for the lattice constants of *a*, *b*, and *c* are -0.52%, -0.52%, and 0.23%, respectively. The deviation of the predicted volume (207.67 $Å^3$ per unit cell) from the experimental value (209.37 $Å^3$ per unit cell) is only about -0.815%.

The total potential energies from the prediction and experiment are -52.545 eV and -52.53 eV, respectively, giving an negligible error of -0.015 eV, or an relative error of ~0.03%. The corresponding enthalpy of reaction is predicted to be exothermic, in agreement with the experimental observation in Ref. [14].

As listed in Table III, all elastic constants are overly predicted but significantly improved compared with the results obtained using the Tersoff mixing potential. In the attempt to reduce the error on the elastic constants for the U_3Si_2 phase, the errors on the potential energies and lattice constants are found to increase. This indicates that some balance is needed between the accuracies of different properties. The current potential paramters are chosen to give the enthalpy of formation correctly and to match the lattice constants as best as possible for the U_3Si_2 phase, with an acceptable level of accuracy for the elastic constants.

Table III. Calculated material properties of U_3Si_2 and U_3Si phases using the parameters listed in the Table I, compared with the dataset from either experiment such as the lattice constants (*a*, *b*, *c*, in Å) [13] and total potential energy *E* (eV) [14] or DFT calculations of the elastic constants C_{ij} (GPa) [15].

Atoms/UC	Phase	Type	Exp./DFT	Ca.	Error (%)
10	U_3Si_2	C_{11}	167.26	249.801	49.35
10	U_3Si_2	C_{33}	205.31	221.611	7.94
10	U_3Si_2	C_{12}	45.63	120.439	163.95
10	U_3Si_2	C_{13}	50.34	154.813	207.53
10	U_3Si_2	C_{44}	67.49	109.251	61.88
10	U_3Si_2	C_{66}	74.09	102.274	38.04
10	U_3Si_2	E	-52.53	-52.545	0.03
10	U_3Si_2	a	7.3364	7.298	-0.52
10	U_3Si_2	b	7.3364	7.298	-0.52
10	U_3Si_2	c	3.89	3.899	0.23
4	h-U_3Si	E	-20.51	-22.218	8.33
4	h-U_3Si	a	4.346	4.381	0.81
4	h-U_3Si	b	4.346	4.381	0.81
4	h-U_3Si	c	4.346	4.381	0.81
16	m-U_3Si	E	-86.15	-88.872	3.16
16	m-U_3Si	a	6.029	6.196	2.77
16	m-U_3Si	b	6.029	6.196	2.77
16	m-U_3Si	c	8.696	8.762	0.76

3.2.2 U_3Si Phase

The lattice constants from the cross-term potential agree well with the experimental values [13] for both h-U_3Si and m-U_3Si phases. Specially, the lattice constants for the h-U_3Si (4 atoms per unit cell) phase is 4.381 Å, corresponding to an error of only -0.81% in reference to the experimental value of 4.346 Å. The cubic symmetry is maintained after being fully relaxed. The error of the predicted volume (84.09 $Å^3$ per unit cell) in reference to the experimental value (82.09 $Å^3$ per unit cell) for the h-U_3Si phase is about 2.436%.

The cubic h-U_3Si structure is metastable when the temperature is below 780 °C [13] and will transform to the tetragonal m-U_3Si phase. As listed in the Table III, the lattice constants of *a*, *b*, and *c* for the m-U_3Si (16 atoms per unit cell) phase are 6.196 Å, 6.196 Å, and 8.762 Å, respectively. The tetragonal structure is kept and the deviation of *a*, *b*, and *c* from the experimental results are 2.77%, 2.77%, and 0.76%, respectively. The error of the predicted volume (336.377 $Å^3$ per unit cell) against the experiment value (316.09 $Å^3$ per unit cell) for the m-U_3Si state is about 6.418%.

With the targeting potential energy of -86.15 eV for the m-U_3Si phase, the value predicted by the cross-term potential is -88.872 eV, with a relative error of 3.16%. The predicted enthalpy of reaction is also exothermic, which is consistent with the experimental observation [14].

The elastic constants are not tested for both phases of U_3Si. We have attempted to improve the potential performance on U_3Si phases regarding the energy and elastic constants. However, this requires a significant sacrifice in the performance for U_3Si_2, which is the primary focus.

In summary, the lattice constants and structure volume for the U_3Si_2 phase and two U_3Si phases predicted by the cross-term potential are in excellent agreement with the experimental data. Compared with the Tersoff mixing potential, significant improvement has been noticed on the elastic constants of U_3Si_2. Improvement is also observed regarding the lattice constants and the enthalpy of formation. Such improvements are likely related to the fact that for the cross-term potential, more parameters are fitted from experimental or DFT data.

3.2.3 Metallic Uranium

Metallic uranium has three solid phases: α (face-centered orthorhombic), β (tetragonal) and γ (body-centered cubic (bcc) [16]. Upon increasing temperature, uranium transforms from α to β [17] at approximately 935 K and β transforms to γ at approximately 1045 K [18]. The transferibility and the accuracy of the unary U potential are tested for all three phases, α, β, and γ. Table IV lists the calculated material properties of α, β, and γ-U using the parameters listed in Table I. During the potential fitting procedure, the data regarding the phase order is aligned with the structure stability in uranium according to Ref. [18, 19]. The corresponding potential energies for β and γ phases are derived from our DFT calculations and data collected in Ref. [20], respectively.

For the αU phase, the data is taken from previous experiments on the lattice constants (Å) [21], the total potential energy (eV) (based on the cohesive energy from Ref. [22]), and the elastic constants (GPa) at 0K [23] from a linear extrapolation of experimental observation [24]. For the βU phase, the lattice constants are from experimental measurements in Ref. [17]. For the γU phase, the lattice constant is from the experiment in Ref [25] at room temperature, 298K.

3.2.3.1 αU phase

For uranium metal, the ground state is the orthorhombic α-phase, with space group of *Cmcm* (#63) [21]. It is stable up to 935 K at ambient pressure [16]. The lattice constants of *a*, *b*, and *c* for the αU phase are predicted to be 3.125 Å, 5.413 Å, and 5.103 Å, respectively. The agreement between the predictions and the experimental data [21] is reasonable with the errors being less than 10.2%. Specially, the errors for *a*, *b*, and *c* are -10.19%, -7.74%, and 3.4%, respectively. The deviation of the predicted volume (86.32 $Å^3$ per unit cell) from the experimental value (82.11 $Å^3$ per unit cell) for the αU phase is about 5.12%. The total potential energies for the 4-atom unit cell of αU given by the potential is -22.32 eV, in reference to a value of -22.2eV derived from the experimental cohesive energy (-5.55 eV/atom) from Ref. [22], with a negligible error of 0.54%.

As listed in Table IV, all elastic constants are under-estimated except for C_{12}. Further improvement on the elastic constants requires some sacrifice in the accuracies regarding the energy and lattice constants. Another attempt to reduce the error of the lattice constants for αU lead to a deviation of relative phase order in reference to that in Ref. [18], and an increase in the errors for the energy and lattice constants.

Table IV. Calculated material properties of the three U phases of (α, β, γ), using the parameters listed in Table I for U, compared with the dataset from either experiment or DFT calculations. For the αU phase, the data are included the lattice constants (Å) [21] and the total potential energy (eV) (based on the cohesive energy from Ref. [22]) and the elastic constants (GPa) at 0K [23] from a linear extrapolation of experimental observation [24]. For the βU phase, the lattice constants are from experiments in Ref. [17]. For the γU phase, the lattice constants are from experiments in Ref [25] at 298K. The potential energies for β and γ phases are derived from the data collected in Ref. [20], in which the phase order is aligned with the structure stability in uranium in Ref [18].

Atoms/UC	Phase	Type	Exp./DFT	Ca.	Error (%)
4	αU	C_{11}	210	177.1	-15.67
4	αU	C_{22}	215	177.08	-17.64
4	αU	C_{33}	297	190.13	-35.98
4	αU	C_{44}	145	49.21	-66.06
4	αU	C_{55}	94	49.21	-47.65
4	αU	C_{66}	87	55.45	-36.26
4	αU	C_{12}	46	66.17	43.85
4	αU	C_{13}	21	53.14	153.05
4	αU	E	-22.2	-22.32	0.54
4	αU	a	2.836	3.125	10.19
4	αU	b	5.867	5.413	-7.74
4	αU	c	4.935	5.103	3.40
30	βU	E	-163.413	-164.49	0.66
30	βU	a	10.759	10.322	-4.06
30	βU	b	10.759	10.714	-0.42
30	βU	c	5.653	5.745	1.63
2	γU	E	-10.339	-10.973	6.13
2	γU	a	3.47	3.474	0.12
2	γU	b	3.47	3.474	0.12
2	γU	c	3.47	3.474	0.12

3.2.3.2 βU phase

β phase, with centro-symmetric space group $P4_2/mnm$ (#136) [17], is stable from 935 to 1045 K [16, 19] for pressures up to 3 GPa [26]. It has a very complicated tetragonal structure with 30 atoms per primitive cell (PC). As listed in Table IV, the predicted lattice constants *a*, *b*, and *c* of βU are 10.322 Å, 10.714 Å, and 5.745 Å, respectively. Note that the tetragonal structure is unstable and transfers to an orthorhombic structure after full structure relaxation. The discrepancies of *a*, *b*, and *c* with respect to the experiment values given in Ref. [17] are -4.06%, -0.42%, and 1.63%, respectively. The error of the predicted volume (635.339 $Å^3$ per unit cell) in reference to the experiment value (654.369 $Å^3$ per unit cell) is about 2.908%.

With the targeting potential energy of -163.413 eV (corresponding to a cohesive energy of -5.447 eV/atom, shifting up those of the αU phase by 0.103 eV/atom according to our DFT calculations), the total potential energy given by the potential is -164.49 eV. The corresponding error is 0.66%. The predicted cohesive energy of -5.483 eV/atom is shifted up by 0.097 eV/atom with respect to αU. Thus the right phase order between αU and βU is attained. The elastic constants are not tested for the βU phase.

In an attempt to reduce the error on the lattice constants for βU, the error on the cohesive energy worsens. Note there are several potentials for the metal U in the literature [20, 27-29], but so far none of them has been applied to the βU phase.

3.2.3.3 γU phase

The bcc γ-U phase is stable from 1045 K to the melting point of 1405 K [16]. The bcc structure can be viewed as the parent phase from which many of the high temperature actinide metal structures are derived, since many actinide metals also have a low-symmetric bcc phase [30] at high temperature.

For γU, the lattice constants are 3.47 Å from experiment [25] at 298K. As listed in Table IV, the predicted lattice constants *a*, *b*, and *c* are 3.474 Å, 3.474 Å, and 3.474 Å, respectively. The cubic structure is kept upon a full relaxation and the deviation of the lattice constants from the experimental value is only 0.12%. The corresponding error of the predicted volume (41.927 Å^3 per unit cell) from the experiment value (41.782 Å^3 per unit cell) is negligible, about 0.346%.

The predicted potential energy is -10.973 eV for the 2-atom unit cell of the γU phase, in reference to the target of -10.339 eV. Correspondingly, the cohesive energies from prediction and the reference value are -5.4865 eV/atom and -5.1695 eV/atom, respectively. As a consequence, the cohesive energy is 0.0935 eV higher with respect to the αU phase and 0.0035 eV lower with respect to the βU phase. This indicates the current unary U potential may not be able to distinguish the phases between the βU and γU thermally at finite temperatures. The elastic constants are not tested for the γU phase.

In an attempt to pursue the transferibility of the fitting potential in order to predict the correct structure stability for the three U phases, the discrepancies of the predicted energy, lattice constants, and elastic constants from the reference data become worse. It is extremly difficult to maxiumize the transferibility and the accuracy of all phases. Some compromise to balance them may be necessary. Here the potential paramters for unary U are chosen to give the correct cohesive energy, lattice constants and unit cell volume.

4. CONCLUSION

To allow for MD simulations to discover the underlying mechanisms of phase transformation and fuel swelling under irradiation on U_3Si_2 fuels, it is critical that the used MD potential is capable to predict the cohesive energies and lattice constants well against experimental data for a variety of second phases besides U_3Si_2 phase. In this work, a Tersoff type bond-order U-Si interatomic potential is developed. In particular, the U-Si potential developed here is based on the unary Si potential existing in the literature and a U potential that is developed here. Two sets of parameters are obtained for U-Si systems using cross-term fitting (the cross-term potential) and the Tersoff mixing rules (the Tersoff mixing potential), respectively. Data from experiments and DFT calculations are used to fit and to assess the fitting results. While both potentials show satisfactory fitting results on the lattice constants and enthalpies of formations for U_3Si_2 and U_3Si phases, the cross-term potential is found to be superior to the Tersoff mixing potential in all areas. The former also produces much better agreement with the literature data on the elastic constants of U_3Si_2. Therefore, the cross-term potential is likely to be the choice for possible further improvement and may probably be used to study mechanical properties with/without irradiation as well.

The unary U potential developed here serves as the basis to obtain a U-Si potential, which is the primary focus. It reasonably reproduces the literature data on the lattice constants and cohesive energies of (α, β, γ)-U phases, showing some transferibility of the potential. However, it fails to predict the right phase order between βU and γU with a negligible energetic difference between them. Therefore, it would hard for this potential to distinguish these two phases at finite temperatures. However, it's not clear if any phase transition will happen if a simulation starts with one of these two phases.

Note that the potential fitting has been limited to some basic material properties of U_3Si_2. Lattice defects such as point defects, their clusters and interfaces have not been included. Part of the reason is that such data are mostly missing. These data will be used to test the robustness once they are available. In order to tackle the fission gas formation and its impact on the fuel swelling, a pair interaction term will be added to the U-Si potential to include fission gas such as Xe.

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