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Simple analytic embedded atom potentials for HCP metals①

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Abstract: A new simple analytic embedded atom model including a modified term, which has previously been successfully applied to the atoms in the FCC and BCC crystal systems, is now extended to the HCP structure. The model parameters are determined for HCP transition metals Co, Hf, Re, Ru, Sc, Ti, Y and Zr with ideal c/a ratios. The model is fitted to the lattice constants, cohesive energy, vacancy formation energy, elastic constants and is able to reproduce the experimental data quite well. The structure stability of real HCP, BCC and simple cubic is discussed, the formation energy of divacancy in the base plane and in different planes are also calculated, and the divacancy is found to be not bound.

Key words: embedded atom method; vacancies formation; energy; structural stability

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1 INTRODUCTION

Daw and Baskes[1] have developed a so-called embedded atom method (EAM). It has been successfully applied to studies of pure metals and alloys[1~5]. Daw, Foiles and Baskes[2] have recently reviewed the literature. More recently many-body potentials have been developed for hexagonal close-packed (HCP) metals[6~8]. These potentials do not include angular dependent term, hence a non-physical embedding energy is required for metals with a negative Cauchy discrepancy. Baskes and Johnson[9] have recently developed a modified embedded atom potential including angular dependence. The model is more complicated in the procedure of determining the parameters and has little applications, especially for alloys of HCP transition metals.

In order to obtain a simple EAM model, which can fit a negative Cauchy discrepancy, the angular dependent term must be included. The model of Baskes and Johnson[9] is complicated in the calculations. So, we proposed a simple EAM model with a modified term in the equation of energy. The introduced modified term is used to describe the effect of angular dependence.

2 MODEL

The simple analytical embedded atom potentials proposed by Ouyang *et al*[10] have been previously applied to studying the BCC and FCC metal systems[10~12]. It has been extended to transition HCP metals. According to the procedure of Ouyang *et al*[10], the energy of a given atom is taken as

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$$E = F(\rho) + \frac{1}{2}\sum_m \phi(r_m) + M(p) \tag{1}$$

$$\rho = \sum_m f(r_m) \tag{2}$$

$$p = \sum_m f^2(r_m) \tag{3}$$

where $F(\rho)$ and $\phi(r)$ are embedding energy and effective two-body potential respectively, $f(r)$ is the electron density distribution function, r_m is the separation distance to the mth neighbor, $M(p)$ is the modified term that was introduced by Ouyang *et al*[10] on the base of the following considerations.

On one hand, according to the conventional EAM concept, the electron density of an atom is of spherical symmetry. As we know, of the electrons out of atomic nuclei, only s-electron has spherical symmetric distribution. The other electrons have a non-spherical symmetric distribution. That means that an angular dependence must be considered as pointed by Baskes *et al*[9], and some modification is necessary. As pointed by Baskes *et al*[13], the angular dependence is related with the square of atomic electron density distribution function. So the modified term is the function of the square of atomic electron density function to descibe the angular dependence. On the other hand, in the procedure of conventional EAM, the host electron density at the position of atom i is a superposition of the atomic electron densities of the neighbors of atom i. This assumption is also simple in an extent for transition metals, and some modification is also necessary. The introduced modified term is considered as description of the effects for above two aspects on the total energy of an atom.

To obtain an EAM model, the form of $F(\rho)$, $f(r)$, $\phi(r)$ and $M(p)$ must be determined. In the present consideration, the embedded function $F(\rho)$ and $f(r)$ take the same forms as those of Johnson[14,15].

$$F(\rho) = -F_0\left[1 - n\ln\left(\frac{\rho}{\rho_e}\right)\right]\left(\frac{\rho}{\rho_e}\right)^n \tag{4}$$

$$f(r) = f_e\left(\frac{r}{r_1}\right)^{\beta} \tag{5}$$

where ρ_e, f_e are, respectively, the values at equilibrium for ρ and f; F_0, β and n are the model parameters. The effective two-body potential $\phi(r)$ is taken as

$$\phi(r) = k_0 + k_1\left(\frac{r}{r_1}\right)^2 + k_2\left(\frac{r}{r_1}\right)^4 + k_3\left(\frac{r_1}{r}\right)^{12} \tag{6}$$

where r_1 is the value of separation distance from the given atom to its nearest neighbor at equilibrium, k_i($i = 0, 1, 2, 3$) are parameters.

The modified term is taken as

$$M(p) = \alpha\left(\frac{p}{p_e} - 1\right)^2 \exp\left[-\left(\frac{p}{p_e} - 1\right)^2\right] \tag{7}$$

where p_e is the value of p at equilibrium, α is the model parameter.

The parameters mentioned above are determined by fitting the model to the cohesive energy, vacancy formation energy, lattice and elastic constants. For HCP metals, which have five independent elastic constants C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, all in Voigt notation. To obtain the relationship between the linear elastic constants (C_{ijkl}) and the EAM parameters, an infinitesimal homogeneous strain are applied to a perfect pure crystal at equilibrium[16] and the elastic constants are given as follows:

$$\Omega C_{ijkl} = B_{ijkl} + F'(\rho_e) W_{ijkl} + F''(\rho_e) V_{ij}V_{kl} + M'(p_e) X_{ijkl} + M''(p_e) Y_{ij}Y_{kl} + E_{ijkl} \tag{8}$$

with

$$V_{ij} = \sum_m f(r_m)\frac{r_{mi}r_{mj}}{r_m} \tag{9}$$

$$Y_{ij} = \sum_m f'(r_m)\frac{r_{mi}r_{mj}}{r_m} \tag{10}$$

$$W_{ijkl} = \sum_m\left[f''(r_m) - \frac{f'(r_m)}{r_m}\right]\cdot\frac{r_{mi}r_{mj}r_{mk}r_{ml}}{r_m^2} \tag{11}$$

$$B_{ijkl} = \frac{1}{2}\sum_m\left[\phi''(r_m) - \frac{\phi'(r_m)}{r_m}\right]\cdot\frac{r_{mi}r_{mj}r_{mk}r_{ml}}{r_m^2} \tag{12}$$

$$X_{ijkl} = \sum_m\left[2f(r_m)f''(r_m) + 2f'(r_m)f'(r_m) - \frac{2f(r_m)f'(r_m)}{r_m}\right]\cdot$$

$$\frac{r_{mi} r_{mj} r_{mk} r_{ml}}{r_m^2} \tag{13}$$

$$E_{ijkl} = \sum_m \big[(1/2)\, \phi'(r_m) + F'(\rho_e)\, f'(r_m) + 2\, M'(p_e)\, f(r_m)\, f'(r_m) \big]\, D_{ijkl} \tag{14}$$

and with

$$\left.\begin{aligned}
D_{ijkl} &= \frac{r_{mi}^2}{r_m}, && i = j = k = l \\
D_{ijkl} &= \frac{r_{mi} r_{mk}}{2\, r_m}, && i = j = l \neq k \\
D_{ijkl} &= 0, && i = j \neq k = l \\
D_{ijkl} &= 0, && i = j \neq k \neq l \\
D_{ijkl} &= \frac{r_{mi}^2 + r_{mj}^2}{4\, r_m}, && i = k \neq j = l \\
D_{ijkl} &= \frac{r_{mj} r_{ml}}{4\, r_m}, && i = k \neq j \neq l
\end{aligned}\right\} \tag{15}$$

where the second subscripts i, j, k, l of r_m represent the Cartesian components of the position vector for the mth atom relative to a given atom at the origin. The equilibrium condition is

$$\sum_m \left[\frac{1}{2} \phi'(r_m) + F'(\rho_e)\, f'(r_m) + 2\, M'(\rho_e)\, f(r_m)\, f'(r_m) \right] \frac{r_{mi} r_{mj}}{r_m} = 0 \tag{16}$$

$$(i = 1, 2, 3;\ j = 1, 2, 3)$$

It should be noted that E_{ijkl} vanishes when the equilibrium condition is used. Considering the form of the embedding function and modified function, $F'(\rho_e) = 0$ and $M'(p_e) = 0$, the equilibrium condition of Eqn.(16), therefore, changes to

$$\frac{1}{2} \sum_m \phi'(r_m) \frac{r_{mi} r_{mj}}{r_m} = 0 \tag{17}$$

Also, from Eqn.(8), the elastic constants are expressed in the following:

$$\Omega C_{ijkl} = B_{ijkl} + F''(\rho_e)\, V_{ij} V_{kl} + M''(p_e)\, Y_{ij} Y_{kl} \tag{18}$$

For simplicity, we postulate that HCP structure has ideal c/a ratio and only the first two neighbors are included. Then the vacancy formation energy can be expressed as follows:

$$6\, \phi(r_1) + 3\, \phi(r_2) = -E_f \tag{19}$$

From Eqns.(17) and (18), we obtain the following equations:

$$6\, r_1\, \phi'(r_1) + 3\, r_2\, \phi'(r_2) = 0 \tag{20}$$

$$r_1^2 f''(r_1) + r_2^2 f''(r_2) + r_2 f'(r_2) = 3\, \Omega C_{44} \tag{21}$$

$$5\, r_1^2\, \phi''(r_1) + 2\, r_2^2\, \phi''(r_2) - r_1\, \phi(r_1) = 6\, \Omega(C_{11} - C_{12}) \tag{22}$$

$$2\, F''(\rho_e) \big[4\, r_1 f'(r_1) + 2\, r_2 f'(r_2) \big]^2 + 2\, M''(p_e) \big[8\, r_1 f(r_1) f'(r_1) + 4\, r_2 f(r_2) f'(r_2) \big]^2 = \Omega(3\, C_{12} - C_{11}) \tag{23}$$

where the primes indicate the derivative to its argument. E_f is the vacancy formation energy. Then the parameters k_i ($i = 0, 1, 2, 3$), F_0 and n can be determined by the following equations, which are derived from Eqns.(1) and (19) ~ (23).

$$k_0 = -\frac{1}{9} E_f + \frac{17\,437\, \Omega C_{44} - 8\,470\, \Omega(C_{11} - C_{12})}{42\,840} \tag{24}$$

$$k_1 = \frac{2\,250\, \Omega(C_{11} - C_{12}) - 5\,067\, \Omega C_{44}}{9\,520} \tag{25}$$

$$k_2 = \frac{161\, \Omega C_{44} - 65\, \Omega(C_{11} - C_{12})}{1\,020} \tag{26}$$

$$k_3 = \frac{80\, \Omega(C_{11} - C_{12}) - 104\, \Omega C_{44}}{5\,355} \tag{27}$$

$$F_0 = E_c - E_f \tag{28}$$

as for the parameter n, it is empirically taken as

$$n = \sqrt{\frac{\Omega B}{A \beta^2 E_f}} \tag{29}$$

where E_c is the cohesive energy, Ω the atomic volume at equilibrium, B the bulk modules, β is empirically taken as 6 for all transition metals, though it is certain that the exact value of β can be obtained by fitting Eqn.(5) to the results of Clementi and Roetti[17], A is

$$A = \frac{2\, C_{44}}{C_{11} - C_{12}} \tag{30}$$

As for f_e in Eqn.(5), for pure metal, it is canceled. We take it as one. Then the parameter α of Eqn.(7) can be determined as follow

$$\alpha = \frac{9\, \Omega(3\, C_{12} - C_{11}) - 2\, n^2 F_0 \beta^2}{16\, \beta^2} \tag{31}$$

The input physical parameters needed in determination of model parameters are listed in

Table 1. There are seven parameters k_i($i = 0$, 1, 2, 3), F_0, n and α, which can be determined from the Eqns. (24) ~ (31) using the input physical parameters. They are listed in Table 2. Therefore the present model for the transition HCP metal is complete.

3 RESULTS AND DISCUSSION

We have given the complete EAM model for transition HCP metals as above. The effective two-body potential of Ti is shown in Fig.1 and is cut off with a cubic spline within a range, which begins at the position of $r = 1.05\, r_2$(r_2 is the distance of the second neighbor) and ends at the position of the third neighbor. The procedures of cutoff for the potential and the electron density functions are the same as those of Ref.[3]. It can be seen that the potential between the first neighbor and the second neighbor is smoother than that of Pasianot and Savino[7].

The embedding function of Ti is demonstrated in Fig.2. This is the typical shape of the embedding function of Johnson[15]. The total energy changing with the distance between the nearest neighbors for Ti is given in Fig.3. For comparison, the result of Rose's equation[18] is also given. One can see from Fig.3 that the present results agree well with those of Rose within the first neighbor distance. Beyond this range, the result of Rose is higher than that of us.

The model has been used to calculate the elastic constants of pure HCP metals with real c/a ratios. The calculated results are given in Table 3. Only three elastic constants C_{11}, C_{12}, and C_{44} are used as input parameters. The calculated elastic constants C_{11}, C_{12}, and C_{44} have differences with experiments because the real c/a ratios are used, but the agreement is very well. The calculated values of C_{13} are bigger than those of experiments, and the calculated C_{33} are smaller than those of experiments. The

Table 1 Input physical parameters

	Co	Hf	Re	Ru	Sc	Ti	Y	Zr	Ref.
a	2.497	3.195	2.760	2.706	3.308	2.951	3.647	3.231	[19]
c	4.069	5.051	4.458	4.282	5.267	4.679	5.731	5.148	[19]
E_C	4.41	6.35	8.09	6.74	3.89	4.87	4.41	6.36	[20]
E_f	1.35	1.80	2.30	1.85	1.15	1.50	1.25	1.70	[4,9]
C_{11}	1.8443	1.1310	3.7500	3.1567	0.6200	1.0500	0.4867	0.9003	[20]
C_{12}	0.9943	0.4810	1.8062	1.3747	0.2480	0.5120	0.1827	0.4623	[20]
C_{44}	0.4440	0.3480	1.0060	1.1310	0.1730	0.2910	0.1520	0.2090	[20]
B	1.172	0.678	2.281	1.907	0.352	0.656	0.258	0.633	[20]

Note: Lattice constants a and c are in angstrom, cohesive energy E_C and vacancy formation energy E_f in eV and elastic constants C_{11}, C_{12}, C_{44} and bulk modules B in eV/cubic angstrom.

Table 2 Calculated model parameters

	Co	Hf	Re	Ru	Sc	Ti	Y	Zr
k_0	-0.011	0.093	0.114	1.261	-0.206	0.046	-0.081	-0.224
k_1	-0.389	-0.705	-1.118	-2.455	-0.104	-0.489	-0.299	-0.180
k_2	0.175	0.302	0.513	0.882	0.090	0.206	0.152	0.118
k_3	0.045	0.066	0.140	0.063	0.055	0.042	0.052	0.058
F_0	3.06	4.550	5.790	4.890	2.740	3.370	3.160	4.660
n	0.504	0.467	0.626	0.553	0.478	0.445	0.435	0.502
α	0.098	-0.015	0.100	0.018	-0.030	0.051	-0.043	0.030

k_i($i = 0, 1, 2, 3$), F_0, α are in eV; n is dimensionless.

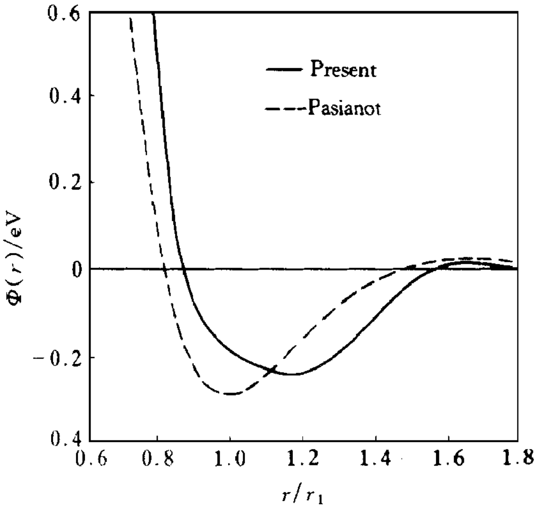

Fig.1 Effective pair potential of Ti

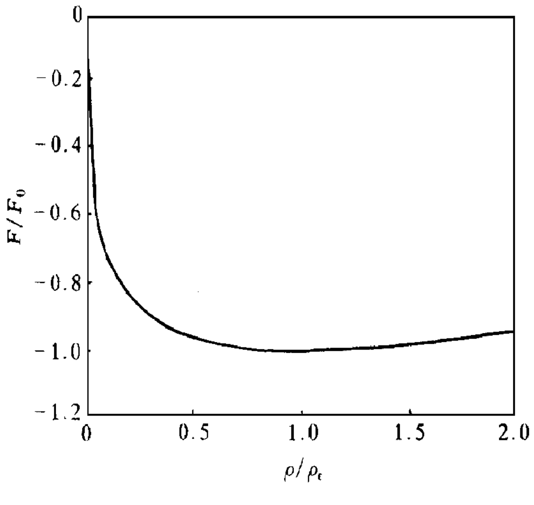

Fig.2 Embedding function of Ti

discrepancies maybe arise from the internal relaxation of HCP structure for its non-central symmetry. In the present calculations, these relaxation effects are not included because the relaxation produce less ten percent changes on the results. It can be seen from that the agreement between the calculations and experiments for C_{13} and C_{33} is, in general, reasonable.

On the other hand, the model has been applied to calculate the difference of energy between the ideal HCP and BCC structure. The results are in general agreement with the experimental data available. It is noted that the real HCP is more stable than ideal HCP. One also can see that the ideal HCP is more stable than BCC and simple cubic. This indicates that the present model can reproduce correctly the stability of structure. From the Table 4, one can see that the present results are in general agreement with those of Baskes *et al*[9].

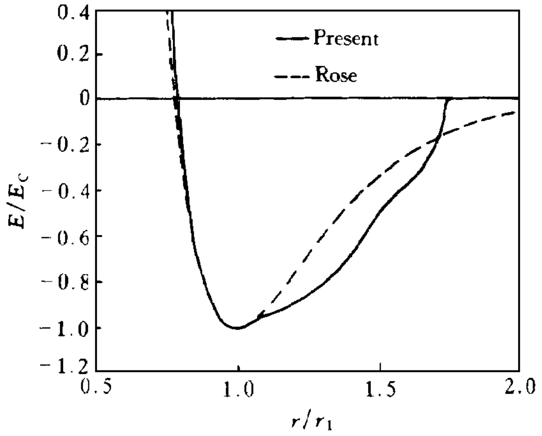

Fig.3 Total energy of Ti calculated with present model and with Rose's equation

The divacancy formation energies for HCP transition metals considered with real c/a ratio have been calculated and are also presented in Table 5. It is noted that the present results are not as accurate as in the vacancy case, because the relaxation of atoms around the divacancy has also not been taken into account, thereby the lattice has larger distortion from perfect lattice. The calculations indicate that the binding energies of divacancy, which are in the same base plane and in different planes, are all negative. Therefore the divacancies are not bonded. The results agree well with those of Baskes *et al*[9].

4 CONCLUSION

A simple analytical EAM model for transition HCP metal has been developed, which includes a modified term. The model parameters are obtained by fitting the cohesive energy, vacancy formation energy, lattice constants, and some elastic constants. The model was used to calculate the elastic constants, vacancy formation and divacancy binding energies, and the energy differences between different structures. The agreement between the calculations and the experimental data available and those of other authors indicate that the present model is successful.

The calculated formation energies for vacancy and divacancy are shown in Table 5. The

Table 3 Calculated and experimental elastic constants, (eV/ cubic angstrom)

	Co	Hf	Re	Ru	Sc	Ti	Y	Zr
C_{11}	1.8375	1.0893	3.6862	3.1282	0.5919	1.0095	0.4617	0.8612
	1.8443	1.1310	3.7500	3.1567	0.6200	1.0500	0.4867	0.9003
C_{12}	0.9903	0.4643	1.7746	1.3523	0.2387	0.4897	0.1756	0.4435
	0.9943	0.4810	1.8062	1.3747	0.2480	0.5120	0.1827	0.4623
C_{13}	1.1066	0.5284	1.8721	1.6461	0.2492	0.5564	0.1973	0.4720
	0.6943	0.4120	1.2870	1.0497	0.1840	0.4120	0.1257	0.4830
C_{33}	1.8339	1.1492	3.7878	2.9323	0.6604	1.0789	0.5089	0.9578
	2.0933	1.2300	4.2690	3.8997	0.6990	1.1320	0.4807	1.0373
C_{44}	0.4459	0.3704	1.0302	1.1531	0.1873	0.3072	0.1673	0.2244
	0.4440	0.3840	1.0060	1.1310	0.1730	0.2910	0.1520	0.2090

Note: The first line is the calculated results and the second line is the experimental data[20] for Cu; and the same for C_{12}, C_{13}, C_{33} and C_{44}.

Table 4 Calculated and experimental values of lattice stabilities (eV) for HCP, BCC and SC (simple cubic) crystal structures relative to HCP with ideal *c/a*

Element	HCP		BCC			SC	
	Calc.	Baskes[9]	Calc.	Baskes[9]	Exp.[21]	Calc.	Baskes[9]
Co	-0.00001	-0.0000	0.092	0.241	-	0.39	0.59
Hf	-0.00462	-0.0059	0.135	0.064	0.059	0.52	0.51
Re	-0.00109	-0.0005	0.250	0.303	0.292	1.13	0.94
Ru	-0.00572	-0.0124	0.282	0.268	0.265	0.57	0.78
Sc	-0.00208	-0.0016	0.068	0.248	-	0.41	0.58
Ti	-0.00248	-0.0071	0.096	0.075	0.070	0.35	0.41
Y	-0.00481	-0.0075	0.082	0.300	-	0.39	0.68
Zr	-0.00212	-0.0105	0.088	0.061	0.076	0.50	0.45

Table 5 Unrelaxation vacancy formation and divacancy binding energies (eV)

	E_f			E_b			
				In-plane		Non-base-plane	
	Calc.	Baskes[9]	Exp.[4,9]	Calc.	Baskes[9]	Calc.	Baskes[9]
Co	1.39	1.48	1.35	-0.1073	-0.47	-0.1413	-0.46
Hf	1.83	2.02	1.80	-0.1636	-0.21	-0.2181	-0.18
Re	1.90	2.49	2.30	-0.1537	-0.63	-0.2636	-0.61
Ru	1.17	2.11	1.85	-0.1326	-0.18	-0.2130	-0.09
Sc	2.39	1.28	1.15	-0.1125	-0.26	-0.1462	-0.25
Ti	1.53	1.80	1.50	-0.1372	-0.13	-0.1724	-0.11
Y	1.27	1.39	1.25	-0.1271	-0.06	-0.1611	-0.03
Zr	1.75	1.93	1.70	-0.1238	-0.53	-0.1850	-0.52

calculated energies are those of a vacancy in crystal with real c/a ratio. It is found that the vacancy formation energy is about 0.1 eV higher than the experimental data. Note that the local atomic relaxation around the vacancy has not been taken into account, so, we can say that these unrelaxed results are in general agreement with those of experiments[4] and those of Baskes *et al*[9].

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