Modified embedded-atom method calculation for the Ni–W system

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A semi-empirical interatomic potential of the Ni–W system was developed using a modified embedded-atom method (MEAM) formalism including second-nearest-neighbor interactions. The cross potential was determined by fitting physical properties of tetragonal Ni_4W available in the literature. The MEAM potential was used to predict phase stabilities, lattice constants, and bulk moduli of nonequilibrium and equilibrium phases in the Ni–W system. The results were in good agreement with experimental information or first-principles calculation.

I. INTRODUCTION

For the last decade, atomistic simulations have been recognized as one of the most important methodologies in materials science that help to interpret physical properties of materials. Molecular dynamics and Monte Carlo simulations, in particular, when combined with semiempirical atomic potentials, make it possible to handle a large number of atoms, up to multimillions.[1] In this case, the accuracy of simulation results depends mainly on the reliability of atomic potentials. Among various semiempirical atomic potentials, the embedded-atom method (EAM) proposed by Daw *et al.*[2] has been very successful in various applications. However, the EAM potential has limitations in describing alloys and compounds because it cannot deal with the elements that have directional bonding characteristics. Baskes proposed the modified EAM (MEAM) including the angular contributions of electron density to describe the directionality of bonding.[3] The original MEAM was formulated to consider only nearest neighbor interactions by using a strong screening function.[4] Recently, Lee *et al.* proposed the MEAM formalism including second nearest neighbor interactions to overcome some critical shortcomings of the original MEAM that usually happen when it is applied to

body-centered-cubic metals.[5,6] In the framework of the second nearest neighbor MEAM (2NN MEAM), it might be possible to describe a wide range of elements using a common formalism.

The Ni–W binary system is of practical importance in both Ni-based superalloys and W alloys. The phase diagram of the Ni–W system shows three equilibrium intermediate compounds (i.e., Ni_4W, NiW, and NiW_2).[7] It is known that Ni_4W has a tetragonal structure with 10 atoms per unit cell ($D1_a$). On the other hand, the structures of NiW and NiW_2 are very complicated, being orthorhombic with 56 atoms per unit cell and tetragonal with 96 atoms per unit cell, respectively. There is little information concerning the physical properties of these intermediate compounds in the literature. The only available information is the result of first-principles (FP) calculation on Ni_4W by Kong *et al.*[8] NiW and NiW_2 are beyond the scope of contemporary FP calculation because of their complicated structures. Kong *et al.*[8] also constructed a semi-empirical atomic potential for the Ni–W system using the formalism proposed by Finnis et al. (F-S).[9] However, with the F-S formalism one cannot distinguish the face-cented-cubic (fcc) and hexagonal-close-packed structures and therefore cannot extend the application to wider range of alloy systems.

The purpose of this work is to apply the 2NN MEAM to the Ni–W system to provide a semi-empirical atomic potential. The MEAM formalism for the alloy system

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and the procedure for the determination of potential parameters to describe the Ni–W system will be outlined briefly. A comparison between the present MEAM calculation and the previous one[8] using the F-S formalism[9] will also be made.

II. FORMALISM

In the MEAM, the total energy of a system is given in the following form:

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

where F_i is the embedding function for an atom i embedded in a background electron density $\bar{\rho}_i$, and $\phi_{ij}(R_{ij})$ is the pair interaction between atoms i and j separated by a distance R_{ij}. For the calculations of energy, the functional forms for F_i and ϕ_{ij} should be given. The background electron density at each atomic site is computed considering the directionality of bonding. A specific form is given to the embedding function F_i, but not to the pair interaction ϕ_{ij}. Instead a reference structure where individual atoms are on the exact lattice points is defined and the total energy per atom of the reference structure is estimated from the zero-temperature universal equation of state by Rose *et al.*[10] Then the value of the pair interaction is evaluated from the known values of the total energy per atom and the embedding energy, as a function of the nearest neighbor distance. In the original MEAM, only first nearest neighbor interactions are considered. The neglect of the second and more distant nearest neighbor interactions is made effective by the use of a strong many-body screening function. The consideration of the second nearest neighbor interactions in the modified formalism is made by adjusting screening parameters C_{min} so that the many-body screening becomes less severe. In addition, a radial cut-off function is also applied to reduce calculation time. The details of the MEAM formalism have been published in the literatures[5,6] and will not be repeated here.

To describe an alloy system, the pair interaction between different elements should be determined. For this, a similar technique that is used to determine the pair interaction for pure elements is applied to binary alloy systems. As for the Ni–W system, a fictitious Ni_3W ordered intermediate compound having an $L1_2$ structure is

chosen as a reference structure. In the Ni_3W structure, the total energy per atom (for ¾ Ni atom + ¼ W atom) is given as follows:

$$\begin{aligned} E^u_{Ni_3W}(R) = {}&\tfrac{3}{4} F_{Ni}(\bar{\rho}_{Ni}) + \tfrac{1}{4} F_W(\bar{\rho}_W) + \frac{Z_1}{2} \left[\tfrac{1}{2}\phi_{NiNi}(R) \right. \\ &+ \tfrac{1}{2}\phi_{NiW}(R) \left] + \frac{Z_2}{2} \left[\tfrac{3}{4}S_{Ni}\phi_{NiNi}(aR) \right. \right. \\ &\left. + \tfrac{1}{4}S_W\phi_{WW}(aR) \right] \quad , \end{aligned} \tag{2}$$

where Z_1 and Z_2 are the numbers of first and second nearest neighbors in the $L1_2$ Ni_3W structure, respectively. In this case, Z_1 and Z_2 are 12 and 6, respectively. S_{Ni} and S_W are the screening function for the second-nearest neighbor interactions between Ni atoms and between W atoms, respectively, and a is the ratio between the second and first nearest neighbor distances in the reference structure.

The pair interaction between Ni and W can now be obtained in the following form:

$$\begin{aligned} \phi_{NiW}(R) = {}&\tfrac{1}{3}E^u_{Ni_3W}(R) - \tfrac{1}{4}F_{Ni}(\bar{\rho}_{Ni}) - \tfrac{1}{12}F_W(\bar{\rho}_W) \\ &- \phi_{NiNi}(R) - \tfrac{3}{4}S_{Ni}\phi_{NiNi}(aR) \\ &- \tfrac{1}{4}S_W\phi_{WW}(aR) \quad . \end{aligned} \tag{3}$$

The embedding functions F_{Ni} and F_W can be readily computed. The pair interactions ϕ_{NiNi} and ϕ_{WW} between the same type of atoms can also be computed from the descriptions of individual elements. To obtain $E^u_{Ni_3W}(R)$, the universal equation of state should be once again considered for $L1_2$ Ni_3W as follows:

$$E^u(R) = -E_c(1 + a^* + da^{*3})e^{-a^*} \quad , \tag{4}$$

where d is an adjustable parameter and

$$a^* = \alpha(R/r_e - 1) \quad , \tag{5}$$

and

$$\alpha = \left(\frac{9B\Omega}{E_c} \right)^{1/2} \quad . \tag{6}$$

r_e is the equilibrium nearest neighbor distance, E_c is the cohesive energy, B is the bulk modulus, and Ω is the equilibrium atomic volume. The parameters E_c, r_e (or Ω), B, and d of $L1_2$ Ni_3W composing the universal equation of state are assumed or determined by experiment or FP calculation. Then, the pair interaction between Ni and W is determined as a function of the interatomic distance R.

III. DETERMINATION OF POTENTIAL PARAMETERS

In the present work, the 2NN MEAM parameters for Ni and W were taken from those proposed by Lee[11] and Lee *et al.*,[6] respectively (see Table I). As described in Sec. II,

TABLE I. Set of the MEAM potential parameters for Ni and W. The units of the cohesive energy E_c, the equilibrium nearest neighbor distance r_e, and bulk modulus B are eV, Å, and 10^{12} dyne/cm^2, respectively.

	E_c	r_e	B	A	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$	C_{max}	C_{min}	d
Ni	4.45	2.49	1.876	0.94	2.56	1.5	6.0	1.5	3.1	1.8	4.36	2.80	0.81	0.05
W	8.66	2.74	3.142	0.40	6.54	1.0	1.0	1.0	−0.6	0.3	−8.7	2.80	0.49	0.00

the extension of the MEAM to alloy systems involves the determination of pair interaction between different types of atoms. The main work in describing alloy systems using the MEAM is to estimate the potential parameters for the universal equation of state for the reference structure. Equations (4)–(6) show that the potential parameters are E_c, r_e (or Ω), B, and d. The first three are material properties. If the reference structure is a real phase structure that exists on the phase diagram of the relevant system, experimental data can be directly used. Otherwise, FP calculation data could be used, if available, or assumptions should be made. The fourth parameter d is a model parameter. In the original literature[10] for the universal equation of state, this parameter was given a value of 0.05 for all materials, which was determined by fitting to the thermal expansion of Cu. However, in the recent MEAM,[6] it has been decided to give either of the two values, 0.05 and 0, according to $\partial B/\partial P$ of individual materials. When the reference structure is not a real phase, it is difficult to estimate a reasonable value of d of the alloy system. For such alloy systems, d is given an average value of those for pure elements.

Besides the parameters for the universal equation of state, there are two more model parameters that should be determined to describe alloy systems. One is the C_{min} value. As can be seen in Table I, each element has its own value of C_{min}. C_{min} determines the extent of screening of an atom (k) to the interaction between two neighbor atoms (i and j). For pure elements, the three atoms are all the same type (i-k-j = A-A-A or B-B-B). However, in the case of alloys, one of the interacting atoms and/or the screening atom can be different type (there are four cases: i-j-k = A-B-A, B-A-B, A-A-B, and A-B-B). Different values of C_{min} may have to be given to each case. Another model parameter is the atomic electron density scaling factor ρ_0. For an equilibrium reference structure ($R = r_e$), the value of all atomic electron density becomes ρ_0. This is an arbitrary value and does not have any effect on calculation for pure elements. Any arbitrary value can be given to an element in calculation for pure elements. However, for alloy systems, especially for systems where the composing elements have different coordination numbers, the scaling factor (relative difference) might give a great effect on calculations.

The above nine model parameters E_c, r_e, B, d, C_{min}, and ρ_0 (there are four binary C_{min} parameters) should now be determined to describe the alloy system. The optimization of the model parameters is performed by fitting physical properties of the alloy system. The physical properties of the Ni–W system available in the literature are experimental lattice constants of Ni_4W,[7] cohesive energy and bulk modulus of Ni_4W by first principles calculation,[8] and lattice constants, cohesive energy and bulk modulus of fictitious phases, $L1_2$ and $D0_{19}$ Ni_3W and NiW_3, by first principles calculation.[8] The heat of formation of the Ni-rich fcc solid solution phase by a CALPHAD-type thermodynamic assessment work is also available.[12] As mentioned already, the fictitious $L1_2$ Ni_3W structure has been chosen as a reference structure, because the structures of the real phases Ni_4W, NiW, and NiW_2 are too complicated. The two parameters, r_e and B of the reference structure $L1_2$ Ni_3W were determined so that lattice constants and bulk modulus of Ni_4W could be well reproduced. The parameter E_c of $L1_2$ Ni_3W was determined so that the cohesive energies of the stable (Ni_4W) and fictitious ($L1_2$ and $D0_{19}$ Ni_3W and NiW_3) phases as well as the heat of formation of the Ni-rich fcc solid solution could be well reproduced at the same time. The C_{min} parameters for Ni–W–Ni and W–Ni–W were optimized to adjust the lattice constant ratio (c/a) of Ni_4W. The C_{min} parameters for Ni–Ni–W and Ni–W–W have been set to prevent a negative thermal

TABLE II. Set of the MEAM potential parameters for the Ni–W system optimized in the present work. The units of the cohesive energy E_c, the equilibrium nearest neighbor distance r_e, and bulk modulus B are eV, Å, and 10^{12} dyne/cm², respectively.

	Selected value	Procedure for the determination
E_c	$0.75\ E_c^{Ni} + 0.25\ E_c^{W} + 0.08$	Fitting
r_e	2.557	Fitting
B	3.189	Fitting
D	$0.75 d^{Ni} + 0.25 d^{W}$	Assumption
C_{min} (Ni–W–Ni)	0.81	Fitting
C_{min} (W–Ni–W)	0.52	Fitting
C_{min} (Ni–Ni–W)	2.25	Fitting
C_{min} (Ni–W–W)	2.25	Fitting
ρ_0	$\rho_0^{Ni} = \rho_0^{W} = 1$	Assumption

TABLE III. Physical properties of various structures in the Ni–W system calculated based on the present MEAM potential in comparison with experiment,[7] FP calculation,[8] and F-S potential calculation.[8]

	a (Å)				c (Å)			E_c (eV)			B (GPa)		
	Exp	FP	MEAM	F-S	Exp	FP	MEAM	FP	MEAM	F-S	FP	MEAM	F-S
$D1_a Ni_4W$	5.73	···	5.73	5.74	3.553	···	3.553	5.40	5.36	5.36	293	292	311
$L1_2 Ni_3W$	···	3.58	3.62	3.58	···	···	···	5.65	5.58	5.74	287	319	340
$L1_2 NiW_3$	···	3.84	3.86	3.76	···	···	···	7.55	7.29	7.73	283	316	399
$D0_{19} Ni_3W$	···	2.53	2.56	2.54	···	4.05	4.15	5.42	5.59	5.58	289	316	338
$D0_{19} NiW_3$	···	2.76	2.76	2.77	···	4.44	4.38	7.70	7.36	7.08	304	321	269

expansion of Ni_4W along the c axis that looked unreasonable to the authors. The remaining d and ρ_0 have been properly assumed due to the lack of relevant information. Table II summarizes the MEAM parameters for the Ni–W system optimized in the present work.

IV. DISCUSSION

Table III compares the physical properties calculated from the present MEAM potentials with those from experiment[7] or FP calculation[8] and the F-S potential constructed by Kong *et al.*[8] The cut-off radius used for the energy calculation is 4.5 Å, which fully covers the second nearest neighbor interactions. When considering the error of FP calculation (about 10%), it can be said that the present MEAM potential predicts the physical properties of all the fictitious ordered structures as well as those of the stable phase, reasonably well. For the transferability of an empirical potential, any calculated physical quantity using the potential should not show too large deviation from experimental data or from high-level calculations. From this point of view, it is thought that the transferability of the present MEAM potential is satisfactory.

The stabilities (heat of formations) of the compound phases listed in Table III are plotted in Fig. 1 in comparison with those of fcc solid solutions. Here, the
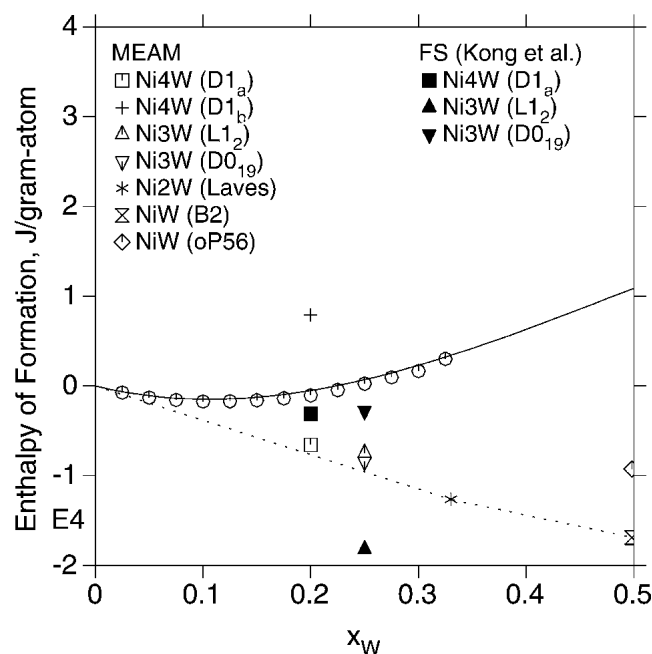

FIG. 1. The calculated heat of formations of stable and unstable compound phases in Ni–W binary system at 0 K, using the present MEAM potential and F-S potential by Kong *et al.*[8] (various symbols). The dotted line represents the stability criterion according to the present MEAM calculation. The calculated heat of formations of the Ni-rich fcc solid solutions by the present MEAM (symbol "O") and by CALPHAD calculation[12] (solid curve) are also presented.

stabilities of other compound phases, $D1_b$ Ni_4W, Ni_2W (Laves phase), B2 NiW, and oP56 NiW computed using the present MEAM potential, are also plotted. The dotted line in Fig. 1, which connects the Ni-rich fcc solution, Laves phase (Ni_2W), and B2 NiW phase, represents the equilibrium phases at 0 K. That is, the present MEAM potential for the Ni–W binary system predicts Laves phase and B2 NiW phase as stable phases at 0 K. According to experiments, the stable compound phases in the same composition range should be $D1_a$ Ni_4W and oP56 NiW.[7] In Fig. 1, the vertical distance between the heat of formation of $D1_a$ Ni_4W and the dotted line, which represents the stability criterion, is quite small. This means that according to the present potential the $D1_a$ Ni_4W phase is almost stable. Concerning the stability of the oP56 NiW phase, it should be noted here that actually the crystallographic structure of the real $Ni_{50}W_{50}$ compound phase is not exactly known. Information in Ref. 7 shows that this phase has the same prototype with the MoNi compound phase whose composition (53 at.% Mo) is different from that of NiW (49.6 at.% W). In the present calculation of the heat of formation of the oP56 NiW phase, fixing the composition at 50 at.% W, the most stable atomic structure was sought simply by exchanging the locations of some of Ni and W atoms based on the atomic structure of the MoNi compound phase. Therefore, the computed value should be thought to be approximate.

In Fig. 1 the results obtained by Kong *et al.*[8] using the F-S potential are also compared. Here, the heat of formation values are those computed based on consistent cohesive energy values for elements, −4.435 eV for Ni[13]
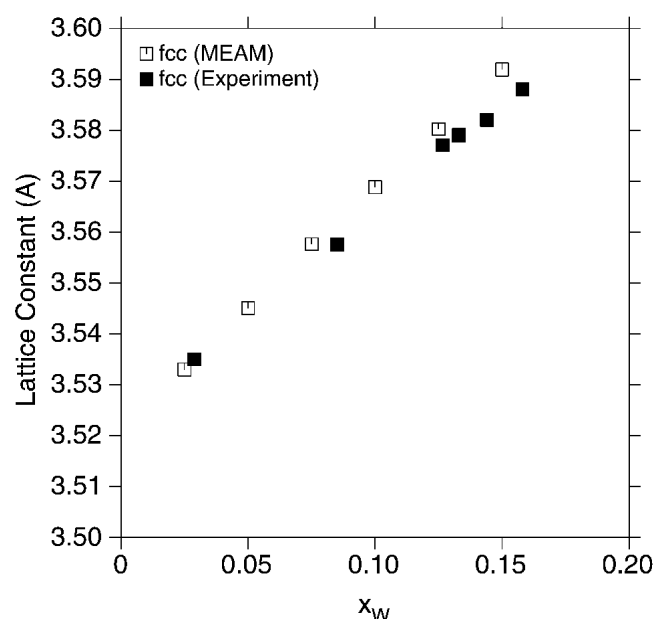

FIG. 2. The calculated lattice constants of the Ni-rich fcc solid solutions at 0 K, in comparison with experimental data.[7]

and −8.90 eV for W.[9] When applying the stability criterion again to these results, it is seen that the $L1_2$ Ni_3W phase is much too stable compared to the real phase $D1_a$ Ni_4W.

The calculation of properties of the Ni-rich fcc solid solutions was performed for $8 \times 8 \times 8$ disordered fcc unit cells (2048 atoms) at 0 K. When the atomic fraction of W was above 0.35, converged values for the energy and location of atoms could not be obtained. The present authors believe this comes from the mechanical instability of fcc W, because according to the present MEAM potential,[6] the fcc W is mechanically unstable. The calculated heat of formations of the Ni-rich fcc solid solutions are presented in Fig. 1, in comparison with the CALPHAD calculation.[12] Figure 2 shows the calculated lattice constant of the Ni-rich fcc solid solutions. The lattice constant increases linearly with increasing W content, following the Vegard's law. The calculated ones are in good agreement with experimental data.[7]

V. SUMMARY

The present 2NN MEAM applied to the Ni–W system shows good agreement with FP calculation in predicting the physical properties of the nonequilibrium phases such as $L1_2$ Ni_3W, $D0_{19}$ Ni_3W, $L1_2$ NiW_3, and $D0_{19}$ NiW_3 as well as the equilibrium phase such as $D1_a$ Ni_4W. The relative stability among nonequilibrium and equilibrium phases is reasonably consistent with experimental phase diagram of the system. It is believed that the present MEAM potential will be useful for further molecular dynamics and Monte Carlo simulations handling many atoms with more practical purposes.

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