Modified embedded-atom method interatomic potentials for the Fe–Nb and Fe–Ti binary systems

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A semi-empirical interatomic potential formalism, the second-nearest-neighbor modified embedded-atom method (2NN MEAM), has been applied to obtain interatomic potentials for Fe–Nb and Fe–Ti systems based on the previously developed potentials for pure Fe, Nb and Ti. The present potentials generally reproduce the fundamental physical properties of the Fe–Nb and Fe–Ti systems accurately. The potentials can be easily combined with already-developed MEAM potentials for binary carbide or nitride systems and can be used to describe Fe–(Ti,Nb)–(C,N) multicomponent systems.
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Niobium or titanium are well-known carbonitride formers. Niobium or titanium carbides and nitrides are important precipitates for strengthening steels. To obtain the desired mechanical properties of steels, it is important to understand the physical metallurgical phenomena such as precipitation, growth of precipitates and the interaction between precipitates and dislocations. All those phenomena are rather difficult to directly examine experimentally, but can be investigated relatively easily if atomic-scale simulation/calculation techniques are used. First-principles calculations provide the most reliable information on atomic-scale or subatomic-scale materials properties. Indeed, many first-principles calculations have been devoted to the metal/carbide or metal/nitride interfaces [1–8]. However, due to the size (or number of atoms) limit, it is often not possible to investigate precipitation behavior using only first-principles calculations. Another approach is to use (semi-)empirical interatomic potentials, which can deal with more than a million atoms. Here, it is important that the interatomic potential should be able to reproduce correctly various fundamental physical properties of relevant materials systems.

Even with the great need for large-scale atomistic simulations on Fe–(Nb,Ti)–(C,N) systems, little research activity has been devoted to the development of (semi-)empirical interatomic potentials for relevant systems. This is because of the difficulty in developing interatomic potentials for multicomponent Fe–(Nb,Ti)–(C,N) systems where the constituent elements, Fe (or Nb), Ti, C and N, differ greatly from each other. To deal with the Fe–Ti–C or Fe–Ti–N system, for example, one needs a potential model that can describe all the constituent elements simultaneously using a common mathematical formalism. However, most of interatomic potential models are mainly for a single type or similar types of elements. From this point of view, the modified embedded-atom method (MEAM) [9] interatomic potential is highly applicable, because it can describe a wide range of elements (body-centered cubic (bcc), face-centered cubic (fcc), hexagonal close-packed (hcp), diamond and even gaseous elements) using a common formalism. The MEAM was created by Baskes [9], by modifying the EAM [10] to include the directionality of bonding. In the original MEAM [9], interactions among only first nearest-neighbor atoms were considered. Recently, the MEAM was modified again by one of the present authors and Baskes (2NN MEAM [11,12]) to partially consider second-nearest-neighbor atom interactions and to remove some critical shortcomings in the original MEAM.

The (2NN) MEAM potential formalism has already been applied to develop interatomic potentials for pure bcc [12], fcc [13], hcp metals [14], carbon [15], gaseous elements (H, N, O) [9] and also for the Fe–C [16], Fe–N [17], Ti–C [18], Ti–N [18], Nb–C [19] and Nb–N [19] binary systems. Since all binary parameters are

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necessary to describe a multicomponent system, the development of Fe–Ti and Fe–Nb binary potentials is required in order to realize atomistic simulations on the Fe–(Nb,Ti)–(C,N) ternary or higher order systems. Such an effort is made in the present work.

In MEAM, the total energy of a system is approximated as

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

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 energy calculations, the functional forms for F_i and ϕ_{ij} should be given. The background electron density at each atomic site is computed by combining several partial electron density terms for different angular contributions. 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. [20]. 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.

To describe an alloy system, the pair interaction between different elements should be determined. For this, a similar technique as is used to determine the pair interaction for pure elements [9] is applied to binary alloy systems. That is, a binary reference structure, where one type of atom has only the same type of atoms as second-nearest-neighbors [12,13], is chosen. The total energy per atom of the reference structure is again computed using the universal equation of state. Then, the pair interaction between different elements is obtained from the known values of the total energy per atom and the embedding energy of the reference structure. The MEAM formalism for pure elements and binary systems is fully documented in the literature [9,11–14,16,21] and will not be repeated here.

For a binary system, 13 model parameters, E_c, r_e, B, d, ρ_0, four C_{min} and four C_{max} should be determined. E_c, r_e, B are the cohesive energy, equilibrium nearest-neighbor distance and bulk modulus of the binary reference structure, respectively. d and ρ_0 are adjustable parameters related to the $(\partial B / \partial P)$ value of the binary reference structure and electron density ratio between individual elements, respectively. C_{min} and C_{max} are parameters that determine the degree of many-body screening [21]. The values of all the potential parameters are deter-

mined by fitting known physical properties of relevant alloy systems. When the effect of a parameter on properties considered is negligible, an assumed default value is given.

The MEAM for an alloy system is based on the MEAM potentials of the constituent elements. In the present work, MEAM interatomic potentials for pure Fe, Nb and Ti were taken from Lee et al. [12] and Kim et al. [14] without any modification (see Table 1).

Each of the Fe–Nb and Fe–Ti binary system has two intermetallic compounds, C14 type Fe_2Nb and Fe_2Ti (laves phase), $D8_5$ type Fe_7Nb_6 and B2 ordered FeTi, on the phase diagram. Since CALPHAD [22,23] type thermodynamic assessments have been carried out for these systems [24,25], the enthalpy of formation of all intermetallic compounds and bcc solid solution, and the enthalpy of mixing of liquids were available. The experimentally reported lattice parameters [26,27] of all intermetallic compounds and Fe–rich bcc alloys were also available. The elastic constants of the FeTi compound [28] were also valuable experimental information for parameter optimization.

None of the two compounds, Fe_2Nb and Fe_7Nb_6, in the Fe–Nb system could serve as an adequate reference structure for the MEAM parameter optimization. This was because those compounds do not meet the criterion that the reference structure for a binary system should be a structure where one type of atom has only the same type of atoms as second-nearest-neighbors. Further, the structure of the Fe_7Nb_6 compound was too complex to describe using an empirical potential, so it was not considered further. In the present work, an $L1_2$ type $FeNb_3$ compound was arbitrarily chosen as the reference structure for the Fe–Nb system. Since no experimental or higher-level calculation data was available for this compound, the potential parameters E_c, r_e and B that correspond to the cohesive energy, equilibrium nearest-neighbor distance and bulk modulus of the $L1_2$ $FeNb_3$ phase, respectively, could not be determined directly. The E_c value was optimized so that the enthalpy of formation of Fe_2Nb, bcc alloys and the enthalpy of mixing of liquids are best reproduced simultaneously. Similarly, the value of r_e was optimized so that the lattice parameters of the Fe_2Nb and bcc alloys are best reproduced. The B parameter value could not be determined since no information on the bulk modulus of Fe–Nb alloys was available. On the other hand, in previous works on the Fe–Pt [29] and Cu–Zr [30] MEAM potentials, it had been found that the bulk moduli of reference structures approximated by taking a weighted average of the values for pure elements are close to first-principles values. Therefore, in the present work, the bulk modulus of the reference structure ($FeNb_3$) was approximated as a

Table 1. Parameters for the MEAM potentials of Fe, Nb and Ti

	E_c	r_e	B	A	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$	C_{min}	C_{max}	d
Fe	4.29	2.480	1.730	0.56	4.15	1.00	1.00	1.00	2.60	1.80	−7.20	0.36	2.80	0.05
Nb	7.47	2.860	1.730	0.76	5.08	1.00	2.50	1.00	1.70	2.80	−1.60	0.36	2.80	0.00
Ti	4.87	2.920	0.968	0.70	2.30	1.00	6.50	1.00	3.50	0.10	−10.0	1.00	1.44	0.00

The units of the cohesive energy E_c, the equilibrium nearest-neighbor distance r_e and the bulk modulus B are eV, Å and 10^{12} dyne cm^{-2}, respectively. The reference structures Fe, Nb and Ti are bcc, bcc and hcp, respectively.

Table 2. Parameter sets for the MEAM potentials of binary Fe–M (M = Nb,Ti) systems

	Fe–Nb	Fe–Ti
Reference state	L12_FeNb$_3$	BCC_B2
E_c	$0.25E_c^{Fe} + 0.75E_c^{Nb} + 0.045$	$0.5E_c^{Fe} + 0.5E_c^{Ti} - 0.22$
r_e	2.837	2.58
B	1.73	1.89
d	$0.25d^{Fe} + 0.75d^{Nb}$	$0.5d^{Fe} + 0.5d^{Ti}$
$\rho_0^{Fe}:\rho_0^{M}$	1:1	1:1
C_{min} (Fe–M–Fe)	1.00	1.21
C_{min} (M–Fe–M)	$0.36(= C_{min}^{Nb})$	0.78
C_{min} (Fe–Fe–M)	$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Nb})^{1/2}]^2$	$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$
C_{min} (M–M–Fe)	$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Nb})^{1/2}]^2$	$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$
C_{max} (Fe–M–Fe)	$2.80(= C_{max}^{Fe})$	$2.80(= C_{max}^{Fe})$
C_{max} (M–Fe–M)	$2.80(= C_{max}^{Nb})$	2.80
C_{max} (Fe–Fe–M)	2.80	2.80
C_{max} (M–M–Fe)	2.80	2.80

The units of the cohesive energy E_c, the equilibrium nearest-neighbor distance r_e and the bulk modulus B are eV, Å and 10^{12} dyne cm^{-2}, respectively.

weighted average (1:3) of those for pure Fe and Nb. Among the eight C_{min} and C_{max} parameters, only C_{min} (Fe–Nb–Fe) was found to have any effect on the calculated properties considered, and the value was adjusted to better reproduce the enthalpy of mixing of liquids.

For the Fe–Ti system, the B2 FeTi compound could serve an adequate reference structure. Since all necessary information, i.e. the enthalpy of formation, lattice parameter and elastic constants of FeTi, was available, the E_c, r_e and B parameter values could be determined directly from corresponding property values, even though a small adjustment was subsequently necessary to better describe other properties. Some C_{min} and C_{max} parameters were given non-default values to better describe the enthalpy of formation or mixing of Fe$_2$Ti or other solution phases.

Table 2 shows the finally determined MEAM parameter sets for the Fe–Nb and Fe–Ti binary systems. The 2NN MEAM formalism includes up to second-nearest-neighbor interactions. Therefore, the radial cutoff distance during atomistic simulations should be at least larger than the second-nearest-neighbor distance in the structures under consideration. All calculations for the Fe–Nb system were performed with a radial cutoff distance of 4.0 Å, according to the radial cutoff distance of the larger element, Nb [12]. Similarly, calculations for the Fe–Ti system were performed with a radial cutoff distance of 4.8 Å, the radial cutoff distance of Ti [14]. The 2NN MEAM calculations are not affected by the size of radial cutoff distance, once it is larger than the third-nearest-neighbor distance of the relevant materials [12].

The MEAM results for lattice parameters of Fe$_2$Nb, Fe$_2$Ti and FeTi are compared with experimental data in Table 3, where a similar comparison is also made for the elastic constants of FeTi. The enthalpy of formation of all compounds considered and Fe-rich bcc alloys, the lattice parameter of Fe-rich bcc alloys and the enthalpy of mixing of liquids in individual systems are compared with relevant experimental information in Figures 1 and 2. It should be noted that the present potential overestimates the C_{44} value of FeTi. An attempt was made to improve this point during parameter optimization, but this could not be achieved without losing the good agreement obtained for the other properties.

Table 3. Calculated lattice parameters of individual compounds, in comparison with experiments

Compound	Property		Exp.	MEAM
Fe$_2$Nb (C14)	Lattice parameter[a]	a	4.81–4.87	4.876
		c	7.85–7.94	7.918
	Unit cell volume		182–187	188
Fe$_2$Ti (C14)	Lattice parameter[b]	a	4.769–4.804	4.76
		c	7.745–7.849	7.70
	Unit cell volume		176–181	174
FeTi (B2)	Lattice parameter[b]		~2.969–2.988	2.98
	Elastic constants[c]	B	1.89	1.89
		C_{11}	3.25	2.74
		C_{12}	1.21	1.47
		C_{44}	0.69	1.69

The units of the lattice parameter, unit cell volume and elastic constant are Å, Å^3 and 10^{12} dyne cm^{-2}, respectively.
[a] Ref. [26], and references therein.
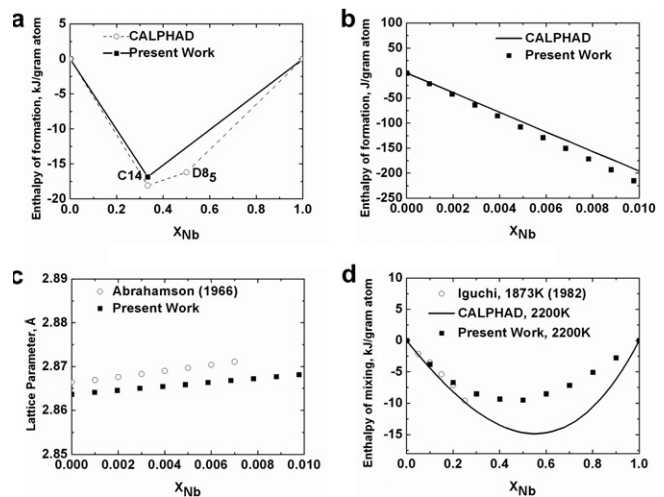[b] Ref. [27], and references therein.
[c] Ref. [28].

Figure 1. Calculated physical properties of the Fe–Nb system. (a) Enthalpy of formation of individual compounds, (b) enthalpy of formation of Fe-rich bcc solution, (c) lattice parameter of Fe-rich bcc solution, and (d) enthalpy of mixing of liquids, in comparison with thermodynamic assessment [24] and experimental data [31,32].
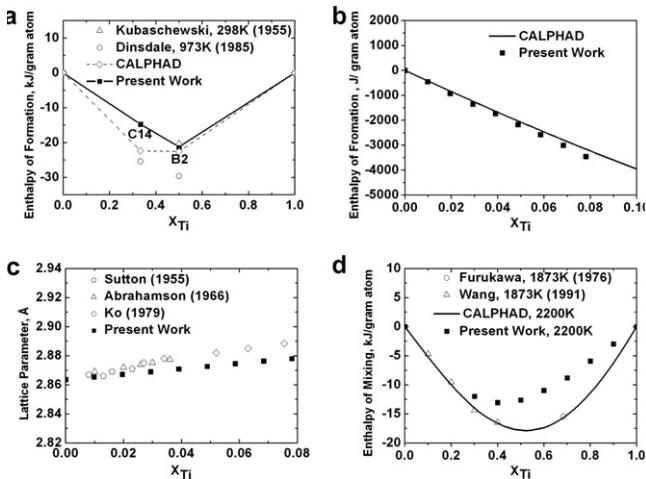
Figure 2. Calculated physical properties of the Fe–Ti system. (a) Enthalpy of formation of individual compounds, (b) enthalpy of formation of Fe-rich bcc solution, (c) lattice parameter of Fe-rich bcc solution, and (d) enthalpy of mixing of liquids, in comparison with thermodynamic assessment [25] and experimental data [31,33–38].

The enthalpy of mixing of liquids is also somewhat underestimated by the present potentials in both systems. Any improvement in this parameter was accompanied by a worsening agreement in the enthalpy of formation of bcc alloys. More weight was given to reproducing solid properties well, considering the purpose of the present work, and description of liquid properties was sacrificed when both solid and liquid properties could not be reproduced well simultaneously.

In summary, it has been shown that the present potentials generally reproduce accurately the fundamental physical properties of the Fe–Nb and Fe–Ti systems. The Fe–Nb and Fe–Ti potentials can be easily combined with already-developed MEAM potentials for the (Fe,-Ti,Nb)–(C,N) carbide or nitride systems, and can be used for atomistic studies on the behavior of carbides or nitrides in Fe–(Ti,Nb)–(C,N) alloys.

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