Calphad 59 (2017) 131–141

Contents lists available at ScienceDirect

Calphad

journal homepage: www.elsevier.com/locate/calphad

Second nearest-neighbor modified embedded-atom method interatomic potentials for the Pt-M (M = Al, Co, Cu, Mo, Ni, Ti, V) binary systems

Jin-Soo Kim, Donghyuk Seol, Joonho Ji, Hyo-Sun Jang, Yongmin Kim, Byeong-Joo Lee*

Dept. of Material Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

ARTICLE INFO

Keywords:
Interatomic potentials
2NN MEAM
Pt alloys

ABSTRACT

Interatomic potentials for Pt-M (M = Al, Co, Cu, Mo, Ni, Ti, V) binary systems have been developed on the basis of the second nearest-neighbor modified embedded-atom method (2NN MEAM) formalism. The parameters of pure Mo have also been newly developed to solve a problem in the previous 2NN MEAM potential in which the sigma and α-Mn structures become more stable than the bcc structure. The potentials reproduce various materials properties of alloys (structural, thermodynamic and order-disorder transition temperature) in reasonable agreements with relevant experimental data and other calculations. The applicability of the developed potentials to atomistic investigations for the shape and atomic configuration of Pt bimetallic nanoparticles is demonstrated.

1. Introduction

Platinum on carbon supports is currently being utilized as catalysts for proton exchange membrane fuel cells (PEMFC). To reduce the amount of expensive Pt or to enhance the catalytic properties over pure Pt, Pt bimetallic nanoparticles have been investigated by many researchers worldwide. For instance, alloying Al, Cu, Co, Mo, Ni, Ti, V with Pt showed a great improvement in the catalytic activity [1–4].

Predicting catalytic performance is essential to design new Pt bimetallic nanoparticles. In order to do that, the shape and atomic configuration in Pt bimetallic nanoparticles should be known. The worldwide efforts have identified a variety of synthesis procedures that enable the production of Pt bimetallic nanoparticles with various shapes and atomic configurations [5]. However, nanoscale structures are generally sensitive to experimental conditions and synthesis-structure-performance relationships are not well understood [6]. In order to reveal the synthesis-structure-performance relationships, atomic-scale simulations are appropriate. For instance, one can calculate shape and atomic configuration in Pt bimetallic nanoparticles at a given temperature and composition using atomistic simulations such as Monte Carlo (MC) and Molecular Dynamics (MD). The atomistic simulations can also be used for exploring alloying elements that may change the equilibrium shape and atomic configuration in Pt bimetallic or tri-metallic nanoparticles for an enhancement of catalytic properties.

The most accurate method of atomistic simulations for calculating materials properties at an atomic level is first-principles calculations. However, first-principles methods cannot calculate large-scale materials properties due to its size (or number of atoms) limit. In case of a nanoparticle of which size is around several nanometers, the simulation should be able to cover at least several thousands of atoms. Therefore, using (semi-) empirical interatomic potentials which can deal with up to several millions of atoms can be a good alternative. In this case, one needs an interatomic potential which can describe various fundamental materials properties (structural, surface, thermodynamic properties, etc.) of the relevant materials correctly.

Due to the importance of (semi-) empirical atomistic simulations, many researchers have developed interatomic potentials for Pt binary alloy systems: modified embedded atom method (MEAM) potential [7] and second-moment approximation of the tight-binding (TB-SMA) [8] for Pt-Co, EAM potential [9] for Pt-Cu, MEAM potential [10] for Pt-Mo, EAM [11], MEAM [12] and tight-binding Ising model area-preserving map (TBIM-APM) [13] for Pt-Ni. In addition to the above potentials, Zhou et al.'s EAM potential database [14,15] may be mentioned since it cover all elements dealt with in the present work except the vanadium and binary alloy systems between the elements. However, it is not known how well those binary potentials describe fundamental materials properties of individual binary alloys. It should be also mentioned here that EAM potentials have mostly dealt with FCC elements and MEAM potentials estimate the relative size of surface energy among low-index surfaces incorrectly [9,12,16]. Also, the tight-binding models have shown unsatisfactory results for bcc elements [17,18]. This difficulty can be overcome by using the 2NN MEAM which reproduces the surface energy anisotropy in FCC elements correctly and describes various elements including FCC, BCC and HCP elements using a single formalism.

The purpose of the present work is to develop the Pt-M (M = Al, Co, Cu, Mo, Ni, Ti, V) interatomic potentials based on the 2NN MEAM as a

* Corresponding author.
E-mail address: calphad@postech.ac.kr (B.-J. Lee).

http://dx.doi.org/10.1016/j.calphad.2017.09.005
Received 1 September 2017; Received in revised form 23 September 2017; Accepted 26 September 2017

Table 1
2NN MEAM potential parameter sets for pure Pt, Al, Co, Cu, Mo, Ni, Ti and V. The units of the cohesive energy E_c, equilibrium nearest-neighbor distance r_e, and bulk modulus B are eV, Å and eV/ Å^3, respectively. The reference structure for Pt, Al, Cu and Ni is FCC, for Co, Ti is HCP and for Mo, V is BCC.

	E_c	r_e	B	A	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$	C_{min}	C_{max}	$d^{+,a}$	$d^{-,a}$
Pt	5.77	2.770	1.7999	0.90	4.92	2.20	6.00	2.20	3.94	−2.20	3.84	1.53	2.80	0.05	0.05
Al	3.36	2.860	0.4955	1.16	3.20	2.60	6.00	2.60	3.05	0.51	7.75	0.49	2.80	0.05	0.05
Co	4.41	2.500	1.2157	0.90	3.50	0.00	0.00	4.00	3.00	5.00	−1.00	0.49	2.00	0.00	0.00
Cu	3.54	2.555	0.8862	0.94	3.83	2.20	6.00	2.2	2.72	3.04	1.95	1.21	2.80	0.05	0.05
Mo	6.81	2.725	1.6557	0.61	5.95	9.00	3.00	1.00	2.00	7.75	−7.00	0.82	2.50	0.00	0.00
Ni	4.45	2.490	1.1708	0.94	2.56	1.50	6.00	1.50	3.10	1.80	4.36	0.81	2.80	0.05	0.05
Ti	4.87	2.920	0.6846	0.66	2.70	1.00	3.00	1.00	6.80	−2.00	−1.20	1.00	1.44	0.00	0.00
V	5.30	2.625	0.9800	0.73	4.74	1.00	2.50	1.00	3.30	3.20	−2.00	0.49	2.80	0.00	0.00

[a] d^+ is for attractive region ($R > r_e$) and d^- for repulsive region ($R < r_e$).

part of a long-term project for an investigation of the synthesis-structure-performance relationship for Pt bimetallic nanoparticle catalysts. This article is organized as follow: in Section 2, we present the procedure for the determination of potential parameters. In Section 3, the reliability of the developed potentials is examined by comparing calculated physical properties with available experimental or first-principles calculations and a brief conclusion in the last section.

2. Interatomic potential

The detailed formalism of 2NN MEAM had been published in literature [19–22] and will not be repeated here, but is presented as a Supplementary material.

2.1. Development of unary potential for Mo

The 2NN MEAM binary system is based on potentials of constituent unary systems. Thus, the development of the Pt-M (M = Al, Co, Cu, Mo, Ni, Ti, V) binary potentials requires potentials for pure Pt, Al, Co, Cu, Mo, Ni, Ti and V. 2NN MEAM potentials for all the relevant pure elements are already developed [20,21,23,24]. However, unary potential for Mo was developed again in the present work since the previous 2NN MEAM Mo potential [20] has a problem in which the sigma and α-Mn structures are more stable than the bcc at 0 K. Table 1 presents the potential parameters of all the pure elements considered in this study including the newly developed Mo potential parameters. Table 2 shows calculated fundamental materials properties of bcc Mo using the present potential, in comparison with reference data and calculations using the previous potential [20]. The problem of the previous Mo potential was solved and all the other materials properties calculated using the present Mo unary potential, are not significantly different from the previous ones.

2.2. Development of binary potential

To describe a binary system, the 2NN MEAM needs 14 independent parameters: E_c, r_e, B and d (or d^+ and d^-), four C_{min} and four C_{max}, and the ratio between the atomic electron density scaling factor (ρ_0^A/ρ_0^B). In addition to the 14 parameters, a reference structure should be defined in the 2NN MEAM. The reference structure is a perfectly ordered binary intermetallic compound, where one type of atoms has only the same type of atoms as second nearest neighbors. E_c, r_e, B and d are cohesive energy, nearest-neighbor distance, bulk modulus and $\partial B/\partial P$ of the reference structure, respectively. These parameters can be determined first, independently from the other parameters based on experimental or first-principles data. The $L1_2$ (Pt_3Al, Pt_3Co, $PtCu_3$, $PtNi_3$, Pt_3V) or B2 (PtTi) is selected as the reference structure depending on the availability of experimental or first-principles information. On the other hand, although three intermetallic compounds ($D0_{19}$ Pt_5Mo_3, B19 PtMo, and $MoPt_2$–type Pt_2Mo) exist on the phase diagram of Pt-Mo system, the structures of those compounds are not suitable for the use as a reference structure. A hypothetical $L1_2$ Pt_3Mo was selected as the reference structure for this system. Since the experimental information necessary for the determination of the parameter d ($\partial B/\partial P$ of the reference structure) was not available, a default assumed value (the average of those for pure elements) was given to this parameter, except for the Pt-V system. The remaining parameters, four C_{min}, four C_{max} and the atomic electron density scaling factor ρ_0^A/ρ_0^B, were determined by fitting to fundamental materials properties of intermetallic compounds and/or solution phases from experiments or first-principles calculations. During the parameter optimization, the existence of an unintentional structure as a stable phase was examined at 0 K and at finite temperatures. Table 3 shows the finally determined potential parameter sets for the individual binary systems.

3. Calculation of materials properties

Calculated materials properties of Pt-M (M = Al, Co, Cu, Mo, Ni, Ti, V) binary alloys are compared with relevant experimental data or theoretical data obtained from first-principles calculations to check the reliability of the potentials. All calculations except for Pt-Al and Pt-Ti systems are performed with a radial cutoff distance of 4.5 Å which is larger than second nearest neighbor distance of Pt, the element with the largest interatomic distance in relevant binary alloy systems. Radial cutoff distances used for Pt-Al and Pt-Ti are 6.0 and 4.8 Å, respectively.

Table 2
Calculated fundamental properties of bcc Mo using the present 2NN MEAM potential, in comparison with experimental data and calculated values using the previous 2NN MEAM potential. Values listed are elastic constants C_{11}, C_{12}, C_{44} (10^{12} dyne/cm^2), structural energy difference ΔE (eV/atom), vacancy formation energy E_v^f (eV), activation energy of vacancy diffusion Q_D (eV), surface energy E_{100}, E_{110}, E_{111} (erg/cm^2), thermal expansion coefficient ε (10^{-6}/K), specific heat C_p (J/mol K), melting point (K) and heat of melting ΔH_m (kJ/mol). The experimental value for surface energy is average surface energy of polycrystal Mo.

Property	Expt.	2NN MEAM	
		Previous [20]	Present
C_{11}	4.647 [41]	4.649	4.748
C_{12}	1.615 [41]	1.655	1.605
C_{44}	1.089 [41]	1.088	1.151
$\Delta E_{bcc\rightarrow fcc}$	0.167 [42]	0.158	0.166
$\Delta E_{fcc\rightarrow hcp}$	−0.038 [42]	−0.038	−0.046
$\Delta E_{bcc\rightarrow\sigma}$	–	−0.06	0.058
$\Delta E_{bcc\rightarrow\alpha\text{-}Mn}$	–	−0.005	0.081
E_V^f	3.10 [43]	3.09	3.10
Q_D	4.5 [44]	4.22	4.65
$E_{(110)}$	2877	2885	2847
$E_{(100)}$	(polycrystal)	3130	2947
$E_{(111)}$	[45]	3373	3049
ε (0–100 °C)	5.1 [44]	5.3	6.0
C_p (0–100 °C)	24.1 [44]	25.9	25.6
m.p.	2896 [42]	3100	2964
ΔH_m	37.5 [42]	20.1	20.8