FORMATION ENTHALPIES FOR FCC METAL BASED BINARY ALLOYS BY EMBEDDED ATOM METHOD①

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ABSTRACT The formation enthalpies of 15 binary alloys bearing fcc metals Cu, Ag, Au, Ni, Pd and Pt in the whole composition range were calculated systematically with a general analytic embedded atom method (EAM) model developed by the authors. The results indicated that the calculations are in good agreement with the experimental data available, and with the results calculated using the first principles and other methods. It was also found that the agreement between the experimental data available and the present calculations is better than that between the experimental data and the results calculated by Johnson's analytic EAM model.

Key words formation enthalpy binary alloy embedded atom method

1 INTRODUCTION

The embedded atom method presented by Daw and Baskes[1] has been applied to studying the properties of pure metals and alloys and a great success has been made, especially for the thermodynamic properties of binary alloys[2, 3]. Ouyang and Zhang[3] provided a general analytic EAM model, which had been successfully applied to calculating self-diffusion and the thermodynamic properties for bcc transition metals.

The formation enthalpies of binary alloys bearing Cu, Ag, Au, Ni, Pd and Pt have been studied by many methods[4-7]. The aim of this paper is to test the generality of the present analytic embedded atom method (hereinafter it is abbreviated to EAM) model by applying it to calculating the formation enthalpies of fcc transition binary alloys.

2 MODEL

According to the EAM scheme, the total energy E_t of an ensemble of atoms is

$$E_t = \sum_i F(\rho_i) + \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \varphi(r_{ij}) \quad (1)$$

$$\rho_i = \sum_j f(r_{ij}) \quad (2)$$

where ρ_i is the total electronic density at atom i, $f(r_{ij})$ is the electronic density of atom j at atom i, r_{ij} is the separation between atoms i and j, $F(\rho_i)$ is the embedding energy by embedding atom i into electronic density ρ_i and $\varphi(r_{ij})$ is the effective-potential between atoms.

Two assumptions have been made in usual EAM model, the first is spherical distribution of electrons of atom, the second is the superposition of atomic electronic density; they cause the discrepancy between the calculations and experi-

① Received Dec. 24, 1996; accepted Apr. 29, 1997

ments. The general analytic EAM model of Ouyang *et al*[3] included the above assumptions and described them by introducing a modified term. Then the basic EAM equations change to

$$E_t = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \varphi(r_{ij}) + \sum_i M_i(P_i) \quad (3)$$

$$P_i = \sum_j f^2(r_{ij}) \quad (4)$$

where $M(P_i)$ is the modified term, P_i is the electronic density including the nonspherical distribution of electrons and the deviation from the linear superposition of atomic electronic density. The modified term describes the energy change caused by the nonspherical distribution of electrons and the deviation from the linear superposition of atomic electronic density.

The functions of $F(\rho)$, $\varphi(r)$, $M(P)$ and $f(r)$ have to be defined to determine an EAM model. Take these functions as

$$F(\rho) = -F_0[1 - n\ln(\frac{\rho}{\rho_e})](\frac{\rho}{\rho_e})^n \quad (5)$$

$$\varphi(r) = K_0 + K_1(\frac{r}{r_1})^2 + K_2(\frac{r}{r_1})^4 + K_3(\frac{r_1}{r})^{12} \quad (6)$$

$$M(P) = \alpha(P/P_e - 1)^2 \cdot \exp[-(P/P_e - 1)^2] \quad (7)$$

$$f(r) = f_e(\frac{r_1}{r})^\beta \quad (8)$$

where foot-note indicates equilibrium and r_1 is the value of the nearest neighbor at equilibrium. F_0, $K_i(i = 0, 1, 2, 3)$, α, f_e, β and n are model parameters and determined by fitting lattice constants a, cohesive energy E_c, monovacancy formation energy E_f, and elastic constants C_{11}, C_{12}, C_{44}. The input and model parameters are given in Table 1 and Table 2 respectively.

Take the interaction potential between atoms as Johnson's formula[12]

$$\varphi^{ab}(r) = \frac{1}{2}[\frac{\varphi^a(r)f^b(r)}{f^a(r)} + \frac{\varphi^b(r)f^a(r)}{f^b(r)}] \quad (9)$$

where superscripts a and b indicate a and b atoms respectively. The total energy of binary alloy is calculated by equations (2), (3), (4) and (9). The lattice structure of alloys is fcc. The lattice relaxation is included by calculating with ten iterations.

The potential function $\varphi(r)$ and electronic density distribution function $f(r)$ are cut-off. The starting point is at the second neighbor and ending point is at the third neighbor for potential, however, the starting point is at the fourth neighbor and the ending point is at the fifth neighbor for electronic density to satisfy eq. (9). The cut-off functions are cubic spline function.

The results are little affected by changing the cut-off intervals except Au-Ni and Pt-Ni systems, for which the results changes about 20%.

3 RESULTS AND DISCUSSION

The general analytic EAM model has been applied to calculating the formation enthalpies for binary alloys bearing Cu, Ag, Au, Ni, Pd and Pt. The results are demonstrated in Fig. 1. For comparison, the results of Terakura *et al*[4-6] using the first-principles method, and the results of Johnson[7] with his analytic EAM model and the experimental data available[12] are also given in the figure.

It can be found from Fig. 1 that the results

Table 1 Input physical parameters

Parameter	Cu	Ag	Au	Ni	Pd	Pt	Refs.
a/ Å	3.164 8	4.086	4.078 1	3.523 9	3.890 2	3.923 7	[8]
E_c/ eV	3.49	2.95	3.81	4.34	3.89	5.84	[9]
E_f/ eV	1.30	1.10	1.10	1.41	1.40	1.60	[10]
C_{11}/ eV·Å^{-3}	1.054 8	0.767 7	1.179 6	1.554 1	1.416 8	2.165 8	[11]
C_{12}/ eV·Å^{-3}	0.761 5	0.572 4	0.992 4	0.948 7	1.098 5	1.566 6	[11]
C_{44}/ eV·Å^{-3}	0.471 2	0.282 7	0.265 9	0.773 9	0.447 5	0.477 5	[11]

of systems bearing Cu, Ag and Au are in good agreement with the experimental data available, the results of the first principles and the results of Johnson. Especially for Cu-Au system, the agreement between the present calculation and experimental data is better than that of other meth-

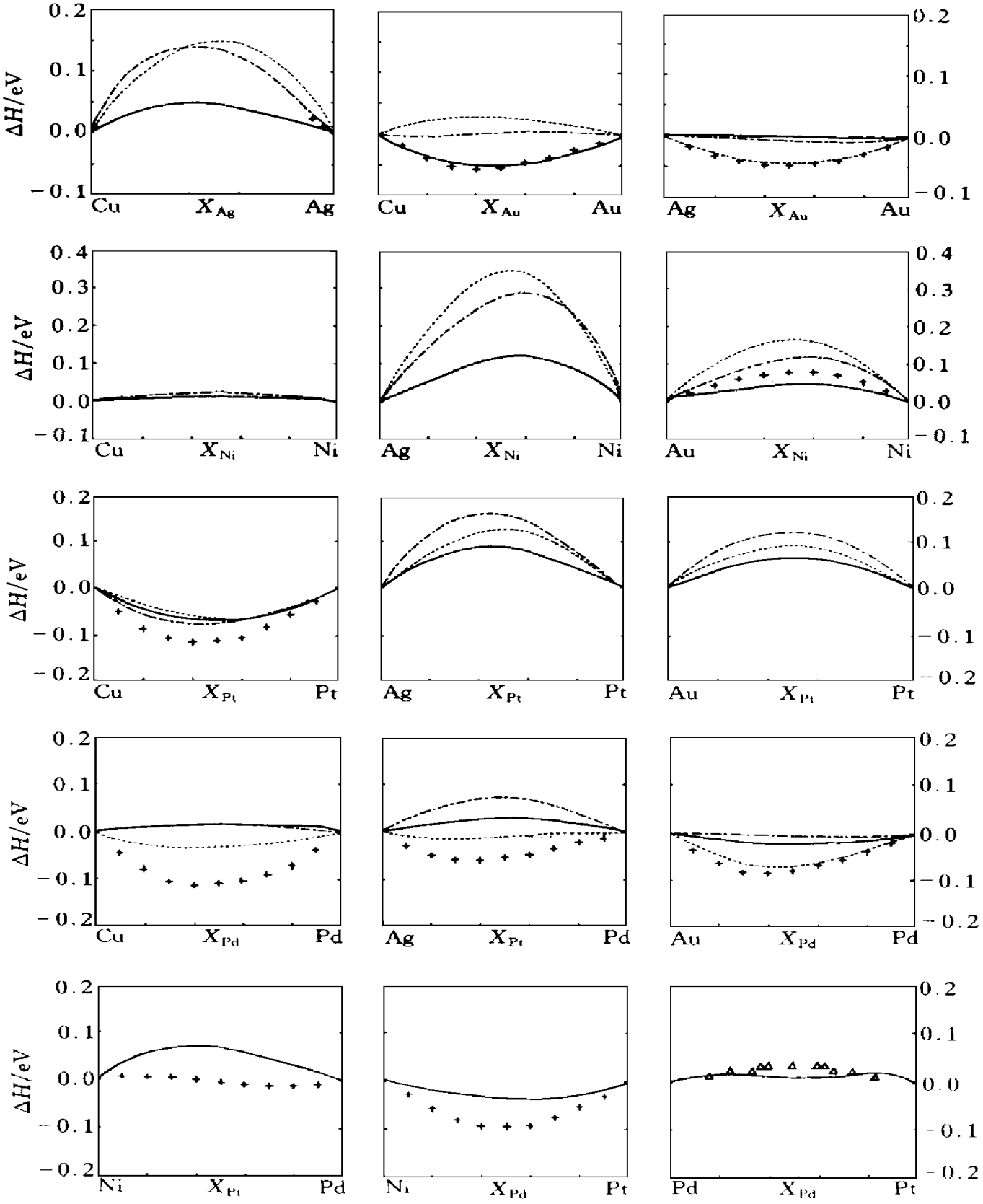

Fig. 1 Formation enthalpies of fcc binary alloys

——present results; —•—results of Johnson[7]; ……results of Terakura *et al*[4-6]; + experimental data[12]; △results of Miedema theory[13]

Table 2 Calculated model parameters

Para.	Cu	Ag	Au	Ni	Pd	Pt
K_0	- 0.615	- 0.509	- 0.478	- 0.778	- 0.671	- 0.469
K_1	0.425	0.338	0.308	0.513	0.445	0.100
K_2	- 0.071	- 0.052	- 0.046	- 0.066	- 0.066	0.051
K_3	0.070	0.060	0.056	0.104	0.082	0.083
F_0	2.190	1.850	2.710	3.03	2.49	4.24
f_e	0.364	0.264	0.333	0.463	0.344	0.467
n	0.260	0.307	0.399	0.311	0.354	0.539
α	0.089	0.134	0.331	0.023	0.260	0.360
β	6	6	6	6	6	6

ods, however, the agreement for Ag-Au is not so good as that of the first principles.

For the six systems consisting of Cu, Ag, Au-Ni and Pt, the present calculations agree well with the results of the first principles, the results of Johnson and the available experimental data. In general, the calculated enthalpies are less than those of Johnson[7], especially for Ag-Ni system.

There are no results for binary alloys bearing Ni, Pd and Pt with the first principles. Johnson also did not give the enthalpies for these systems. There exist experimental data for Ni-Pd and Ni-Pt systems. The curve of the experimental formation enthalpies of Ni-Pd is like *s* shape, however, the calculated results are all positive. The discrepancy may be aroused from constituent Pd, which will be discussed in the following paragraph. The calculated and experimental formation enthalpies for Ni-Pt are all negative, but the calculated values are bigger than the experimental data. For Pd-Pt system, the present calculations are very small, which are in good agreement with the results obtained with Miedema theory[13]. The results indicate the present calculations for the above systems are reasonable.

Among the systems Cu-, Ag- and Au-Pd, the present results of Au-Pd agree well with the experimental data, and agree with the results of the first principles. The agreement with experimental data of the present calculation for Au-Pd is better than that of Johnson's. The results for Cu-Pd and Ag-Pd systems are similar to those of Johnson, and different from the results of Terakura *et al* and of experiments. From the figure, it can be seen that the agreement with experimental data of the present calculations are better than that of Johnson's.

The discrepancies between the calculations and the experimental data, and other calculations for systems including Pd are caused by the description on Pd in the present model. According to the conclusion of Johnson[7], to describe Pd in the EAM procedure, some other properties must be considered except those used to determine the model parameters because of the characteristics of Pd. In the present model, we do not include extra physical properties to describe Pd, so some discrepancy arises. However, the present calculations are more reasonable than those of Johnson because of the introduction of the modified term. This indicates that the present model is more reasonable, to some extent, than that of the analytic model of Johnson.

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(Edited by Peng Chaoqun)