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Study on the Behavior of Additives in Steel Hot-Dip Galvanizing by DFT Calculations

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Two types of additives in hot-dip galvanizing, effective additives Ni, V, and Ti used industrially to reduce the coating thickness of zinc−iron, and noneffective additives Mg, Sn, and Ag showing quite different behavior from the former, were studied with density functional theory calculations by using cluster models. The optimized geometric configurations, total energy, electronic density of states, and electronic charge distributions for the additive−zinc associates were obtained. Results indicated (1) the effective additives have much stronger bonding energy with zinc than the noneffective additives, (2) the electronic charges significantly shift from the zinc atoms to the Ni, V, or Ti atoms, while only a little shift to the Mg, Ag, or Sn atoms occurs, and (3) the Fermi energy level and the band gap of zinc clusters obviously change, owing to adding Ni, V, or Ti, but these effects do not occur for the second type of additives. On the basis of the calculated results, the underlying mechanism of additive effect on the formation of Fe−Zn intermetallics (and/or coating thickness) was proposed.

1. Introduction

Steel hot-dip galvanizing is one of the most important technologies to protect steel from corrosion. It has been reported[1] that each year millions of tons of zinc were used to coat steel with this method. The coating so produced is bonded to the steel by a series of Zn−Fe intermetallics with a layer of almost pure zinc. The thickness of the coating is an important factor affecting the engineering quality of coated materials. To control the coating thickness, a technique which incorporates the additives in the molten zinc bath has been verified as an effective solution to the problem; however, until recently very little has been known about the underlying mechanism of these additives behavior.

This research is a part of our program to design new additives aided by computer modeling and simulation. In our previous study,[2−3] the behavior of some additives was investigated by studying the correlation among fundamental elemental properties, crystal structures, and bulk additive behavior of unary and binary zinc compounds. Two fundamental element properties, melting point (T_m) and pseudopotential atomic radii (R_{s+p}), were recognized as key factors for determining the bulk behavior of additives.[2,3]

On the basis of our previous study, density functional theory (DFT) was attempted to further explore the mechanism of additive behavior in this work. DFT has been validated as a powerful theoretical tool for electronic structure calculations. It has been extensively applied to molecular systems and to modern materials research.[4] The great success with cluster model, a typical DFT method, to simulate solid materials suggests that it is possible to obtain a clearer explanation of additive behavior from atomic scale calculations. With the above idea in mind, the electronic structure calculations for a series of short-range ordering associates of additive and zinc were carried out in this study. The calculations started with the cluster model building for the associates, which might be formed when additives were added into molten zinc bath. The software Faststructure of MSI,[5] which has been shown to be the appropriate DFT computational tool with the relevant compromise between computational cost and accuracy for our materials, was applied to complete the calculations. The geometry configuration, bonding energy, charge distribution, and density of states for different associates were obtained and analyzed. Clearly, the optimized geometric configuration is related to the parameter R_{s+p}, and bonding energy is one property which is closely related to the parameter T_m. On the basis of the analysis of the calculation results, the

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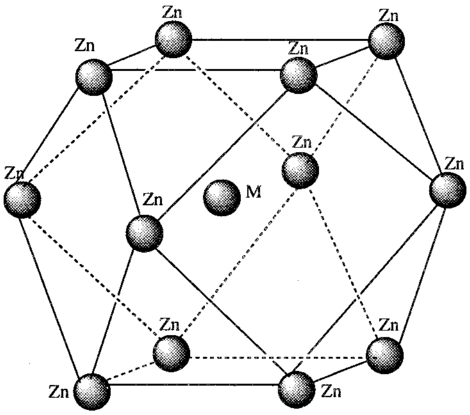

Figure 1. Geometric configuration of cluster model MZn_{12}, M represents Ni, V, Ti, Fe, Sn, Ag, Mg, and Zn, respectively.

underlying mechanism of additives on zinc coatings was proposed.

2. Computation Details

2.1. Cluster Model. The additives investigated in this work are Ni, V, Ti, Mg, Ag, and Sn. Experimental results of galvanizing showed that Ni, V, and Ti could inhibit the growth of Fe−Zn intermetallics, while Mg, Ag, and Sn had minor effect on the intermetallic formation.[6−9] Since the additives are added into the molten zinc bath before steel is dipped into it, the additive-zinc associate might form. The geometric configurations of these associates in the melting state, which are necessary to do DFT calculations, are difficult to be determined exactly due to disorder of liquid structures. As a relative comparison, we assume that reliable results should be obtained if the geometric configuration with same coordinations were used. In our previous research,[3] it was found that most additive−zinc compounds have a common type of 12 coordinations according to the atomic environmental approach.[10] Therefore, to build the cluster model, the ratio of zinc to additive element was defined as 12:1. The geometric configuration to be optimized by DFT was designed in such a way that the total number of 12 Zn atoms were around a central atom of additive element M to form a cuboctahedron structure. The starting-neighbor interatomic distance of the cuboctahedron (listed in Table 2) was the sum of metallic radius of two atoms (Figure 1). Boundary conditions of the cluster models, provided by the software, were considered through wave functions finishing at infinity. In this work seven clusters of MZn_{12} (M represents Ni, V, Ti, Fe, Mg, Ag, and Sn, respectively) were used to simulate the corresponding associates. To measure the electronic structure change of zinc alloy due to the additive effect, Zn_{13} atomic cluster, in which a zinc atom was at the M site, was also calculated.

2.2. Computational Method. DFT is a first principles approach to approximately solve the Schrödinger equation of a multielectron system in an external field, and the energy of multielectron system is given by minimizing the density functional equation which was proposed by Kohn and Sham:

$$E_{ks}[\rho(x)] = T_s[\rho(x)] + E_{es}[\rho(x)] + E_{xc}[\rho(x)] + E_{ext}[\rho(x)] \quad (1)$$

where the terms of the right-hand side refer to the kinetic energy of noninteracting electrons having density $\rho(x)$, the electrostatic energy, the so-called exchange-correlation energy, and the potential energy of noninteracting electrons having density $\rho(x)$ in the external field, respectively.

Table 1. Basis Functions for Metal Element

element	core	valence
Ni	1s, 2s, 2p	3s, 3p, 4s, 3d, 4s', 3d′, 4p
Ti	1s, 2s, 2p	3s, 3p, 4s, 3d, 4s', 3d′, 4p
V	1s, 2s, 2p	3s, 3p, 4s, 3d, 4s', 3d′, 4p
Fe	1s, 2s, 2p	3s, 3p, 4s, 3d, 4s', 3d′, 4p
Mg	1s	2s, 2p, 3s, 3s', 3p
Ag	1s, 2s, 2p, 3s, 3p	4s, 3d, 4p, 5s, 4d, 5s', 4d′, 5p
Sn	1s, 2s, 2p, 3s, 3p, 3d	4s, 4p, 5s, 4d, 5p, 5s', 5p′
Zn	1s, 2s, 2p	3s, 3p, 4s, 3d, 4s’, 3d′, 4p

This is equivalent to solve a set of Kohn−Sham equations comprising of a one-particle Schrödinger equation together with a so-called self-consistency condition:

$$\left\{-\frac{\nabla^2}{2m} + V_{\text{eff}}(x) - \epsilon_n\right\}\phi_n(x) = 0$$

$$V_{\text{eff}}(x) = V_{\text{ext}}(x) + \Phi(\rho(x)) + \mu_{\text{xc}}(\rho(x)) \quad (2)$$

$$\mu_{\text{xc}}(\rho) \equiv \frac{d}{d\rho}[\rho\epsilon^{h}_{\text{xc}}(\rho)]$$

where $V_{\text{ext}}(x)$ is the external field potential, $\Phi(\rho)$ is the Coulomb potential corresponding to $\rho(x)$, $\mu_{\text{xc}}(\rho)$ is the exchange-correlation potential term.

One method of determining energy and force is via the so-called Harris functional:[11]

$$E_h[\rho(x)] = \sum_n a_n\epsilon_n - \int dx\, \rho(x)[{}^1/_2\Phi(x) - \epsilon^{h}_{\text{xc}}(\rho(x)) + \mu^{h}_{\text{xc}}(\rho(x))] \quad (3)$$

In this work, eq 3 is used in conjunction with a trial density form:

$$\rho(x) = \sum_i\sum_v Z_i^v\, \rho_i^v(|x - x_i|) \quad (4)$$

where $\rho\ (|x - x_i|)$ is an atomic centered, spherical symmetric site density and Z is a varied parameter as iterations of SCF. The sum over v allows for a few density basis functional per site. In the present work, one s basis function is used.

The single-particle equation in the eq 2 is achieved by expanding the orbitals, ϕ, in a basis of atomic orbitals (AO’s), which in this work are selected as shown in Table 1.

The form of the exchange-correlation functional, which is used in implementations of local density functional theory, is the analytic expression of BHL (Von Barth, Hedin, and Lundqvist). The occupation number of electrons is distributed by Fermi smearing, and the smearing width is 0.003 Hartree for all the simulated associates.

As shown in eq 1, the accuracy of calculations using DFT depends on the quality of electronic density. To obtain more accurate results, the highest accurate mesh item, FINE, in the software options is used for electronic integration. In addition, the electronic charge density is simultaneously optimized along with the optimization of cluster configuration by using the BFGS scheme[12−15] with adequate convergence (force gradient $<2 \times 10^{-3}$, charge gradient $<4 \times 10^{-3}$ in atomic unit). With BFGS scheme, one would find a local minimum in

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Table 2. Interatomic Distances of MZn_{12}, Zn_{13} before and after Geometry Optimization and Their Experimental Values[a]

compound	D_0	D_s	D_l	D_a	D_{exp}
$NiZn_{12}$	2.57	2.679	2.681	2.680	2.571−2.713
$TiZn_{12}$	2.87	2.815	2.815	2.815	2.721−2.928
VZn_{12}	2.64	2.786	2.789	2.788	2.766−2.988
$FeZn_{12}$	2.58	2.713	2.716	2.714	2.550−2.780
$MgZn_{12}$	2.93	2.928	2.928	2.928	2.914−3.163
$AgZn_{12}$	2.77	2.817	2.817	2.817	2.663−2.820
$SnZn_{12}$	2.74	2.982	2.982	2.982	2.963−3.181
Zn_{13}	2.66	2.869	2.869	2.869	2.660−2.913

[a] D_0 is the sum of metallic radius of two atoms. D_s, D_l, andD_a are the calculated shortest, largest and average interatomic distances between additive and zinc, respectively. D_{exp} is the shortest and largest interatomic distance from experimental data.[15−16] All values are in angstroms.

energy surface corresponding to a stable geometric configuration of the atoms, which is the nearest one to the starting geometry.

3. Calculated Results and Discussions

The optimized geometric configurations, total energy, electronic density of states, electronic charge distribution on each atom were obtained with the calculations. These results would be utilized to discuss the effect of additives on galvanizing.

3.1. Geometric Configuration. In Table 2, three items of interatomic distances (the shortest, the largest, and the average distances) for MZn_{12} and Zn_{13} in their optimized configurations are listed. From Table 2, it can be found that these values are in a reasonable agreement comparing to the data derived from literatures[16,17] (also shown in Table 2). This indicated that the electronic structure information from the optimized configurations is reliable to study the additive behaviors.

3.2. Bonding Energy. The bonding energy ΔE between the additive M and Zn is defined as follows:

$$\Delta E = E_t - E_m - E_{Zn_{12}} \qquad (5)$$

where E_t is the total energy of MZn_{12} system, E_m is the energy of atom M and $E_{Zn_{12}}$ is the total energy of 12 zinc atoms in the corresponding MZn_{12} structures.

The bonding energies calculated according to eq 5 are shown in Table 3. From Table 3 it can be found that the bonding energies between the effective additives M (M = Ni, V, Ti) and Zn are stronger than the bonding energy between Fe and Zn, but the bonding energies between the noneffective additives M (M = Mg, Ag, Sn) and Zn are much weaker.

In galvanizing research, it was proposed that the growth or outburst of iron−zinc alloy formation occurs at the grain boundaries of the substrate at the steel/coating interface.[18] In addition, for process kinetics the one-side diffusion of zinc was reported, unlike the mechanism of two-side diffusion of iron and zinc.[19] On the basis of the bonding energy obtained by our calculations, the additives, which can tightly bond with zinc, may effectively prevent zinc to diffuse into the iron grain boundaries and therefore inhibit iron−zinc growth or outburst structure formation. The calculated bonding energies support the mechanism of one-side diffusion of zinc.[18]

Table 3. Bonding Energy between Center Atom and 12 Zinc Atoms and Net Charge on Zn[a]

	E_t, Hartree	E_m, Hartree	$E(Zn_{12})$, Hartree	ΔE, K cal mol^{-1}	charge of Zn
$NiZn_{12}$	−2883.681	−169.507	−2713.961	−133.659	0.02974
$TiZn_{12}$	−2772.193	−58.030	−2713.972	−119.854	0.02741
VZn_{12}	−2785.482	−71.342	−2713.971	−106.048	0.02588
$FeZn_{12}$	−2837.480	−123.412	−2713.931	−85.9683	0.02838
$MgZn_{12}$	−2777.193	−63.139	−2713.968	−53.9655	0.00158
$AgZn_{12}$	−3306.200	−592.093	−2713.972	−84.7133	0.00089
$SnZn_{12}$	−2926.923	−212.862	−2713.964	−60.8681	0.00628

[a] Abbreviations: E_m, the energy of atom M; $E(Zn_{12})$, the total energy of 12 zinc atoms in the corresponding MZn_{12} clusters; E_t, the total energy of MZn_{12} system.

3.3. Charge Distribution. Since electronic charge density was simultaneously optimized with geometric optimization, charge distributions on each atom reflect an electronic charge shift from the zinc atoms to the additive atoms due to their interactions.

From Table 3, it is interesting to find that the electronic charge of Zn shifts to transition metal additives (Ti, V, Ni) more significantly than to the other additives (Sn, Ag, Mg). This result is in agreement with the tendency of bonding for the associates, which implies that electronic charge shift is an obvious bonding characteristic between effective additives and zinc. Moreover, it can be deduced that the effective additives will grab electronic charges from zinc atoms when they form additive−zinc associates, making it difficult for iron to obtain the electronic charge from zinc later. Therefore, the positive charges on the zinc atoms are like an “anti-iron” wall of the additive−zinc associate to inhibit the formation of Fe−Zn compounds and reduce the coating thickness.

3.4. DOS of Clusters. The calculated DOS of near Fermi energy level for the associates are shown in Figure 2. From Figure 2, the obvious difference of band gap between two types of additives can be found. The band gap is defined as the difference between energy level of HOMO (the highest occupied molecule orbital) and that of LUMO (the lowest unoccupied molecular orbital) according to the cluster simulation method. When electrons occupy Fermi smearing, Fermi energy, which is the output of the software, is defined as the valence band top E(VT) instead of HOMO, but the LUMO could not be clearly determined due to the fact that the electronic charges decreased gradually to zero after Fermi level. To resolve this problem we suggest a definition for the energy level of conduction band bottom E(CB) as

$$E(\mathrm{CB}) = \frac{\sum_i (2 - n_i)\epsilon_i}{\sum_i (2 - n_i)} \qquad (6)$$

where the sum runs from the energy level which is

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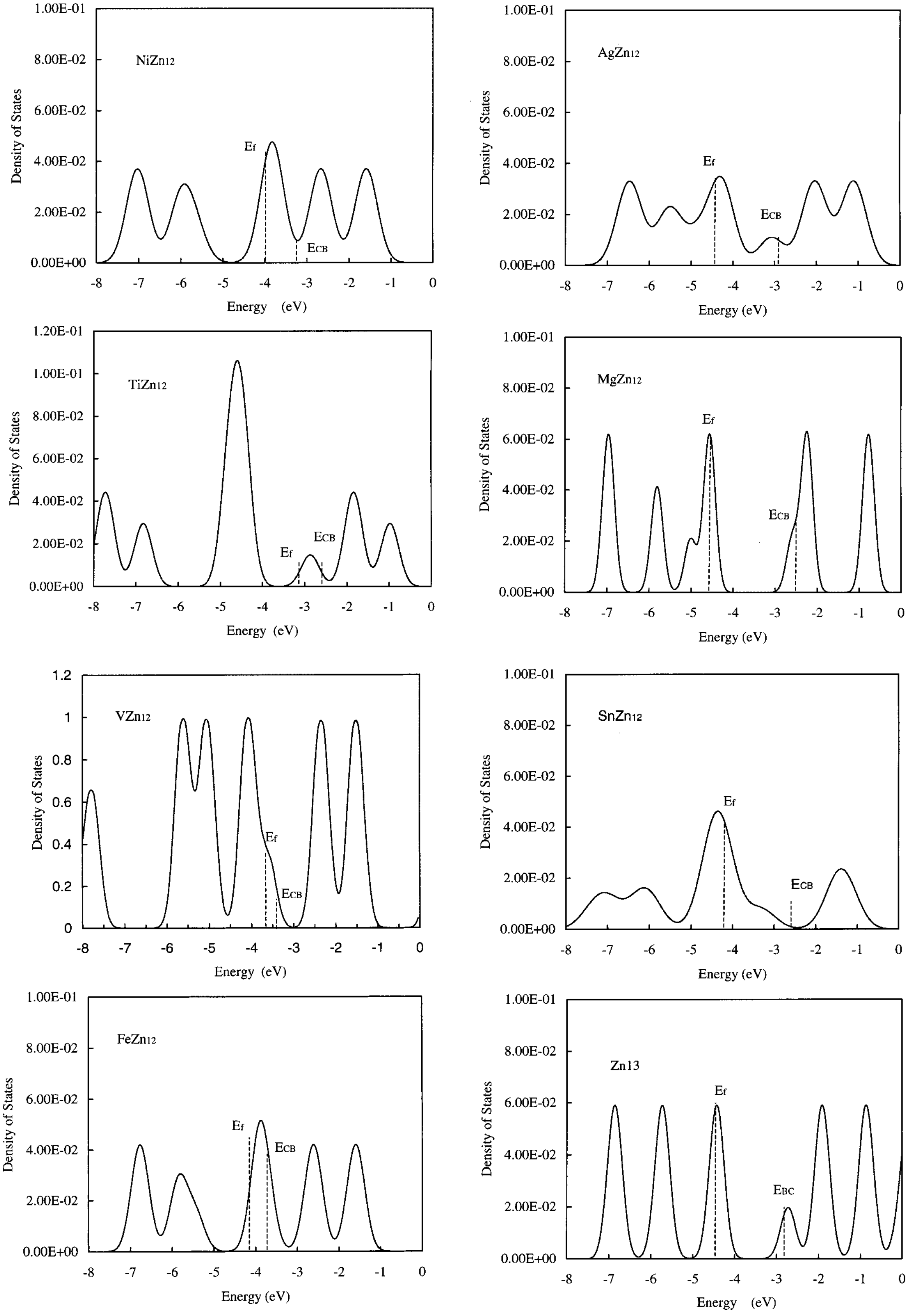

Figure 2. Calculated density of states for additive–zinc associates and Zn_{13}.

higher than Fermi energy level to the first unoccupied level. n_i and ϵ_i are the corresponding electron numbers (max: 2) and energy levels of the occupied states, respectively. In this case, the band gap can be determined as

$$E(\text{gap}) = E(\text{CB}) - E(\text{VT}) \tag{7}$$

Table 4 shows the Fermi energy level and gap of the clusters according to eqs 6 and 7. The narrow gap reveals the characteristic of metallic bond for simulated

Table 4. Fermi Level and Gap of Different Clusters

	E_f, eV	E_{gap}, eV
$NiZn_{12}$	−4.026	0.801
$TiZn_{12}$	−3.143	0.585
VZn_{12}	−3.578	0.259
$FeZn_{12}$	−4.100	0.496
$MgZn_{12}$	−4.455	1.977
$AgZn_{12}$	−4.390	1.583
$SnZn_{12}$	−4.174	1.586
Zn_{13}	−4.421	1.586

associates. It can be found that the difference of Fermi energy level between MZn_{12} (M = Ni, V, Ti) and Zn_{13} is larger than 0.4 eV, and the difference of their gap is larger than 0.7 eV. For additives Ag, Mg, and Sn, the difference is less than 0.25 and 0.39 eV, respectively.

4. Conclusions

The stable geometric configurations of MZn_{12} clusters and their corresponding electronic structure information were obtained by DFT calculations. On the basis of the calculated results, the mechanism of additive effects on controlling the coating thickness of Zn−Fe in hot-dip galvanizing is proposed as the following: (1) stronger bonding in M−Zn (M = Ni, V, Ti) prevents Zn from diffusion to the grain boundary of Fe and (2) since the electronic charges shift to the effective additives, the positive charges on the zinc atoms construct an “anti-iron” wall to resist the formation of Zn−Fe layer. Comparing to the previous results using the correlation method, this work further confirms that galvanizing is a diffusion controlled process concluded by the correlation model and reveals more details of the additive behavior which cannot be delivered by the correlation method. Consequently, it is expected that the current research not only represents theoretical importance, but also can provide a better approach for other materials design, by the combination of two complementary techniques—correlation investigation and quantum mechanics calculations.

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