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Investigation of Additive Effects on Zn Diffusion in Hot-Dip Galvanizing by DFT Calculations

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The DFT calculations of M-Zn_{12} clusters, which model the associates of Zn with 26 additive elements M in hot-dip galvanizing, have been carried out to investigate the additive effects on controlling coating thickness. A discrimination function, consisting of the calculated binding energy of clusters and the chemical shift of zinc 2p energy, is obtained which can predict the effects of additives. It has been further confirmed that an effective additive may intensely attract electronic charge from zinc and greatly grasp zinc atoms to form an associate. The zinc diffusion coefficients in the systems of various additives are estimated, by assuming that the binding energy is proportional to the diffusion activation energy and further the chemical shift is inversely proportional to the pre-exponent factor in the Arrhenius equation. The additive behaviors of six candidate elements are predicted by using the calculated diffusion coefficients. This study may assist in the design of binary and ternary additives since only the Zn diffusion coefficients are to be examined.

1. Introduction

In recent decades a dramatic increase in zinc coating studies of hot-dip galvanizing was observed due to new applications in the automotive and building industries.[1] The thickness of the coating, which is composed of a series of Zn−Fe intermetallics and a layer of almost pure zinc, is a key factor affecting the engineering quality of the coated materials. To control the coating thickness, a proven technique is to incorporate chemical additives in the molten zinc bath. A number of observations, which indicate the effectiveness of additives in controlling coating thickness, were accumulated.[2−4] But the underlying mechanism of the additive effects was not very clear. Recently, a series of studies on the mechanism were conducted,[5−7] and this paper is a part of the efforts. It is intended to explore the mechanism by means of the electronic structure properties obtained by quantum chemical calculations. Moreover, this study is useful to guide the design of binary and ternary additives.

In our recent studies, the correlation among additive behaviors, elemental properties, and crystal structures of binary additive-zinc compounds was established, and a few candidates for effective additives were predicted.[5] Following that, we performed electronic structure calculations to model six types of M-Zn associates (M = Ni, V, Ti, Ag, Sn, and Mg) by density functional theory (DFT).[7] The calculated results showed that the additive effects were attributed to the strong interaction between M and Zn and the charge shift from Zn to M. Moreover, the calculated results also showed that each of the two electronic structure properties, bonding energy and charge shift, could be used to simply identify the additive behaviors of the six elements.

To verify the proposed mechanisms in a large pool of additives, we further investigated all experimentally known additives by using a more exact DFT scheme and a more realistic cluster model. In the present work, the interaction between Zn and M is depicted by the binding energy of the associate, and the charge shift is described by the chemical shift of Zn 2p electronic energy. It is found that the newly calculated two electronic structure properties are still the predominant factors that determine the additive effect for controlling the coating thickness. It is also shown that the correlation between the two electronic structure properties and the zinc diffusion coefficient (with the presence of additives) can be reasonably built up. These results further confirm and elaborate the underlying mechanism of additive effects, which is controlled by the two electronic structure properties of the associates.

The paper is organized as follows. The cluster model for the associates of M-Zn and DFT calculation is presented at first. We then discuss results including discrimination function and the zinc diffusions, and finally the conclusions.

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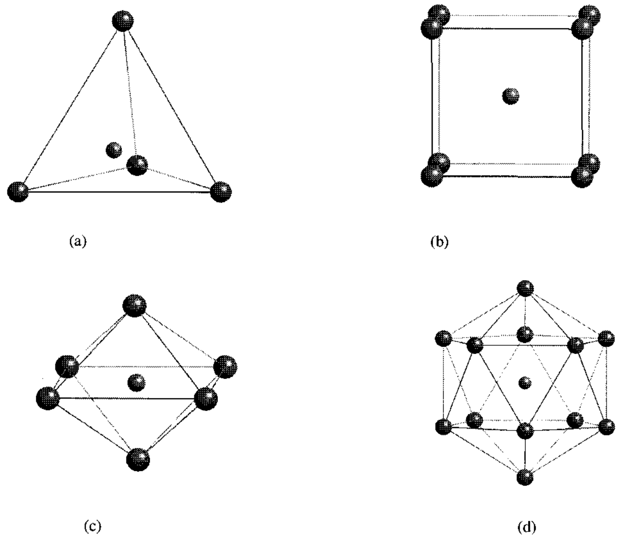

Figure 1. Computational model of additive-zinc associates (a) the tetrahedral MZn4 (b) the hexahedral MZn8 (c) the octahedral MZn6 (d) the icosahedral MZn12.

2. Cluster Model and DFT Calculations

The additive effects of 26 elements are investigated in this work. Among the 26 elements, 8 elements are known to be effective in controlling coating thickness, 12 are ineffective, and 6 are predicted to be potential effective additives on the basis of the previous work.[5]

Since the additives are added into molten zinc bath before steel is dipped into it, according to the structure theory of metallic molten state,[8] which claims that the zinc atoms exist in a cluster, the additive may replace a zinc atom to form a cluster of M-Zn associates. It is difficult to determine exactly the geometric configurations of these clusters in the melting state due to disorder of liquid structures. But the present work merely aims for a systemic comparison among various associates: reliable results may be obtained from a uniform geometric configuration with the same number of coordinates for all additives. In our previous research, it has been found that most additive-zinc compounds have a common type of 12 coordinates according to the atomic environmental approach.[6] In addition, icosahedral structures consisting of 12 coordinates with a center atom have been suggested to be important in disordered systems such as supercooled liquids and glasses.[9] Moreover, with DFT calculations, we examined the relative stability of commonly assumed other three possible configurations including M-Zn_4, M-Zn_6, and M-Zn_8 by comparing with M-Zn_{12} (described in Appendix). Figure 1 depicted the geometrical configuration of four structures, where M is at the symmetric center, and Zn atoms are at the vertexes. Calculation results indicated that the energy is in favor of the icosahedral M-Zn_{12} for all the additive elements. Therefore, in this study, M-Zn_{12} cluster model will be used.

A standard DFT software Dmol3[10,11] is employed to perform the quantum chemical calculations with the following program options: geometry optimization, spin unrestricted, GGA exchange-correlation scheme of nonlocal density functional,[12] double-numerical quality basis set with polarization function, octupole auxiliary density fitting, and scalar relativistic corrections.[13]

The optimization of cluster configuration by using the BFGS scheme [14−17] with an adequate convergence (energy <0.00001 au, force gradient <0.01 au, and maximum displacement <0.01 au). With BFGS scheme, one will find a local minimum in energy surface corresponding to a stable geometric configuration of the atoms, which is the nearest one to the starting geometry.

Cluster binding energy E_b is defined as

$$E_b = E_t - \sum_{at} E_{at} \qquad (1)$$

where E_t is the total energy of cluster and E_{at} is the energy of an isolated atom. The binding energy represents the stability of the associate, including the interactions not only between the additive atom and zinc atoms but also between zinc atoms under the influence of the additive atom.

The 2p energy of zinc atom of cluster M-Zn_{12} can be strictly obtained from Dmol3 relativity calculations. The change of atomic inner shell electron energy, which is the known chemical shift corresponding to the energy spectrum of chemical analysis (ESCA), exactly measures the charge variation of zinc environment due to the various additive atom at the center of cluster.[18] We define the chemical shift as

$$\Delta E_{2p} = E(\text{Zn-Zn}_{12})_{2p} - E(\text{M-Zn}_{12})_{2p} \qquad (2)$$

where the two items in the right of equation are the Zn 2p energy in $ZnZn_{12}$ and M Zn_{12} clusters, respectively. The ΔE_{2p} demonstrates the extent of zinc electronic charge shift owing to additive effect. The more positive the ΔE_{2p}, the more the electronic charge shifts from zinc atom to the additive atom, and vice versa.

Besides 26 associates M-Zn_{12}, the cluster Fe-Zn_{12}, and Zn-Zn_{12} were calculated for references.

3. Calculated Results and Discussions

3.1. Geometric Configuration and Charge Shift. The optimized interatomic distance, Zn 2p electronic energy, cluster binding energy, and chemical shift of zinc 2p obtained from the calculations are listed in Table 1. The optimization results of these clusters show that there exists a stable geometric configuration with the distance of M-Zn close to the sum of their metallic radius. Compared with the literature data, the optimized distances are basically in the range of the experiments[19,20] with maximum deviation of 5% (for Sr, Mg, and La). Due to the disorder of liquid structure, these optimized geometric configurations may be regarded as possible cluster states in zinc bath.

The charge shift representing chemical bonding characteristics is an important electronic structure property. In general, one often deduces the charge shift between

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Table 1. The Calculated Results of Configuration OptimizAtion, Binding Energy, Zinc 2p Energy, Chemical Shift, and the Discrimination Function for the Additive Effects

a	M	*d* (cal)/nm	*d* (exp)/nm	$E(\text{M-Zn}_{12})_{2p}$/hartree	E_b hartree	ΔE_{2p}/hartree	$f(\Delta E_{2p},E_b)$/hartree
1	Al	0.2750	0.2642−0.2863	−38.71091	−0.39448	0.0030	6.01×10^{-02}
	Cr	0.2698		−38.71260	−0.39244	0.0047	8.68×10^{-02}
	Cu	0.2672	0.2566−0.2810	−38.71226	−0.40095	0.0043	8.95×10^{-02}
	Mn	0.2678	0.2601−0.2861	−38.71352	−0.39363	0.0056	1.04×10^{-01}
	Ni	0.2663	0.2571−0.2713	−38.71276	−0.50835	0.0048	2.05×10^{-01}
	Ti	0.2769	0.2721−0.2928	−38.70750	−0.49518	−0.0004	1.03×10^{-01}
	V	0.2730	0.2766−0.2988	−38.71032	−0.49552	0.0024	1.51×10^{-01}
	Zr	0.2883	0.2889−0.3066	−38.70193	−0.50270	−0.0060	1.57×10^{-02}
2	Ag	0.2777	0.2721−0.2853	−38.70742	−0.34601	−0.0005	-4.76×10^{-02}
	Bi	0.3045		−38.69702	−0.30379	−0.0109	-2.67×10^{-01}
	Cd	0.2838	0.2669−0.2920	−38.70406	−0.22913	−0.0039	-2.22×10^{-01}
	Co	0.2658	0.2496−0.2610	−38.71396	−0.50238	0.0060	2.20×10^{-01}
	Ge	0.2786		−38.70813	−0.37686	0.0002	-4.71×10^{-03}
	La	0.3095	0.3256−0.3700	−38.69090	−0.44258	−0.0170	-2.32×10^{-01}
	Mg	0.2770	0.2916−0.3047	−38.70751	−0.31139	−0.0004	-8.08×10^{-02}
	Pb	0.3025		−38.69703	−0.30580	−0.0109	-2.65×10^{-01}
	Sb	0.2948	0.2694−0.2851	−38.70052	−0.33132	−0.0074	-1.80×10^{-01}
	Sn	0.2908	0.2963−0.3181	−38.70358	−0.26538	−0.0043	-1.94×10^{-01}
	Th	0.3073	0.3115−0.3408	−38.69066	−0.47475	−0.0173	-2.04×10^{-01}
	U	0.2916	0.2889−0.3348	−38.69312	−0.59709	−0.0148	-3.97×10^{-02}
3	Hf	0.2853	0.2912−0.3170	−38.70602	−0.51881	−0.0019	1.01×10^{-01}
	Mo	0.2760		−38.71093	−0.40065	0.0030	6.67×10^{-02}
	Nb	0.2810	0.2708−0.2948	−38.70734	−0.47456	−0.0006	7.96×10^{-02}
	Sr	0.3188	0.3370−0.3767	−38.69042	−0.24236	−0.0175	-4.40×10^{-01}
	Ta	0.2762		−38.71187	−0.53888	0.0039	2.21×10^{-01}
	Y	0.2948	0.3133−0.3369	−38.69721	−0.46164	−0.0107	-1.06×10^{-01}
	Zn	0.2737	0.2660−0.2913	−38.70793	−0.31809	0.0000	-6.69×10^{-02}
	Fe	0.2668	0.2550−0.2780	−38.71343	−0.45727	0.0055	1.66×10^{-01}

[a] Numbers 1, 2, and 3 stand for the effective, ineffective, and predicted additives, respectively.

two types of atoms by using the electronegativity concept. Unfortunately, it is quite difficult to define the electronegativity value of metallic elements, especially of the transition metallic elements, because even the famous Mulliken electronegativity does not define them. Discrepancies on reported electronegativity values are commonly observed, such as the data for Zn, Ag, and Al.[21] In this case, it is impossible to use the electronegativity value to elaborately discuss the calculated results of chemical shift. However, it is commonly accepted that zinc is considerably more electropositive than its neighbors in the transition group of the chemical element table.[22] Accordingly, the electronic charge may shift from zinc to its neighbor transition elements when zinc combines with them. The calculated results show that the zinc 2p energies in the clusters with its neighbor transition elements (Cu, Ni, Co, Fe, Mn, Cr, and V) are all lower than that in the cluster ZnZn_{12} (−38.707929 hartree), i.e., the transition elements cause a positive chemical shift. This means that the electronic charge shifts from zinc to the transition elements according to ESCA principles.

3.2. Correlation of the Effects and the Properties. We now turn to discuss the correlation of the additive effects with the electronic structure properties. It can be seen from Figure 2 that a discrimination line can be found to separate the effective additives and ineffective additives except element Co (which will be discussed later on).

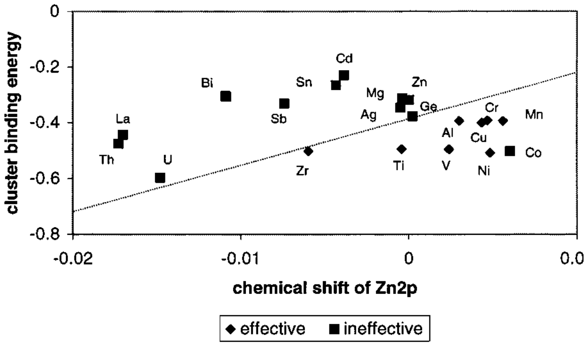

Figure 2. The correlation map between the two electronic structure properties and additive effects. The scales of axes are in hartree.

With the slope (17) and intercept (−0.385) of the discrimination line in Figure 2, a linear function, $f(\Delta E_{2p},E_b)$, describing the discrimination line is obtained to identify the additive effect as follows.

$$\begin{aligned} f(\Delta E_{2p},E_b) &= 17\Delta E_{2p} - E_b - 0.385 \\ f(\Delta E_{2p},E_b) &> 0.0 \text{ effective} \\ [f(\Delta E_{2p},E_b)] &< 0.0 \text{ ineffective} \end{aligned} \tag{3}$$

This function has been tested by 20 additives of known effects (the final column of Table 1).

The slope is dimensionless, but the dimension of $f(\Delta E_{2p},E_b)$ is energy, which is reasonable because the energy problem determines the diffusion of zinc in the interface between zinc and iron, though its details have not been revealed yet. From another point of view, the chemical shift represents the charge shift so that the slope can also be regarded as the dimension of the electrostatic potential E/q. This implies that the change of potential field due to the additives is an essential influence on the zinc diffusion.

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3.3. The Effect on Zinc Diffusion. Although the processing of additives in the zinc bath are quite complex, it has been recognized that the coating thickness essentially depends on the velocity of zinc diffusion between liquid zinc and the surface of iron.[1,2] The fact that the binding energy and charge shift correlate strongly to the additive effects implies that the two electronic structure properties may also correlate to the diffusion of zinc in the bath. The diffusion coefficient can be expressed as a preexponential fact, D_f^0 and activation energy E_a, as in the Arrhenius equation[23]

$$D_f = D_f^0 A \exp(-E_a/RT) \tag{4}$$

The activation energy should be the energy difference between the energy sum of reactants (M-Zn_{12} and Fe) and the energy of some transition state, which is a complicated associate consisting of the M-Zn-Fe complex. The details of the transition state in the zinc bath cannot be measured regardless of theoretical methods or experimental methods in the present case; therefore, as an approximation, we make some assumptions. The first step of zinc diffusion may be the dissociation reaction

$$\text{M-Zn}_{12} \rightarrow \text{M-Zn}_{11} + \text{Zn}$$

In this case, the association energy is related to the activation energy. Then in the second step the associated zinc interacts with the surface of iron, which will reduce the reaction energy. The activation energy is, actually, less than the dissociation energy, but it may be reasonable to assume that the activation energy is proportional to the dissociation energy of the M-Zn_{12} associate. In other words, the activation energy of zinc diffusion may be proportional to the binding energy (absolute value) of M-Zn_{12}. In fact, the dissociation energy for one zinc atom in Zn-Zn_{12} is about 69.6 kJ/mol (the 1/12 of binding energy of Zn-Zn_{12}), which is within the range of the literature data (60−105 kJ/mol).[2,23]

Let us now analyze the correlation between the preexponential factor D_f^0 and the charge shift in various associates. The D_f^0 value depends on the collision frequency between reactant particles. The charge shift leads the surrounding of associate to carry charge and to form an electrostatic field. Due to the positive chemical shift for Fe-Zn_{12}, iron tends to attract the electronic charge away from zinc. Therefore the associates with negative shift may collide more favorably with the surface of iron than those with positive shift do. The preexponential factor A may be approximately regarded to be inversely proportional to the chemical shift.

The measured diffusion data of zinc at 673 K, the preexponential factor $D_f^0 = 3.2 \times 10^{-5}$ m^2 s^{-1} and E_a = 104.6 kJ/mol,[23] are used as the reference to estimate the zinc diffusion coefficients (in the presence of various additives). The activation energy of associate M-Zn_{12} is obtained by

$$E(\text{M-Zn}_{12})_a = 104.6 \frac{E_{b,\text{M-Zn}_{12}}}{E_{b,\text{Zn-Zn}_{12}}} \text{ kJ mol}^{-1} \tag{5}$$

To link the chemical shift data ΔE_{2p} (which may be negative) to the preexponential factor A (which is always positive), we first normalize the chemical shift data within a range from 0.2 to 0.8 for practical reasons.

Table 2. The Calculated Results of Zinc Diffusion Coefficients at the Presence of Additives

M	E_{act}/kJ/mol	D_f^0 m^{2}s^{-1}	$\exp(-E/RT)^a$	D_f/m^2 s^{-1}
Al	$1.297 \times 10^{+05}$	2.86×10^{-05}	1.854×10^{-10}	5.312×10^{-15}
Cr	$1.290 \times 10^{+05}$	2.70×10^{-05}	1.963×10^{-10}	5.306×10^{-15}
Cu	$1.318 \times 10^{+05}$	2.73×10^{-05}	1.584×10^{-10}	4.331×10^{-15}
Mn	$1.294 \times 10^{+05}$	2.62×10^{-05}	1.898×10^{-10}	4.978×10^{-15}
Ni	$1.672 \times 10^{+05}$	2.69×10^{-05}	1.001×10^{-10}	2.691×10^{-15}
Ti	$1.628 \times 10^{+05}$	3.25×10^{-05}	1.002×10^{-10}	3.262×10^{-15}
V	$1.629 \times 10^{+05}$	2.93×10^{-05}	1.002×10^{-10}	2.932×10^{-15}
Zr	$1.653 \times 10^{+05}$	4.19×10^{-05}	1.001×10^{-10}	4.195×10^{-15}
Ag	$1.138 \times 10^{+05}$	3.27×10^{-05}	1.575×10^{-09}	5.143×10^{-14}
Bi	$9.990 \times 10^{+04}$	5.61×10^{-05}	1.773×10^{-08}	9.949×10^{-13}
Cd	$7.534 \times 10^{+04}$	3.77×10^{-05}	1.419×10^{-06}	5.356×10^{-11}
Co	$1.652 \times 10^{+05}$	2.59×10^{-05}	1.002×10^{-10}	2.590×10^{-15}
Ge	$1.239 \times 10^{+05}$	3.17×10^{-05}	3.406×10^{-10}	1.081×10^{-14}
La	$1.455 \times 10^{+05}$	9.71×10^{-05}	1.051×10^{-10}	1.021×10^{-14}
Mg	$1.024 \times 10^{+05}$	3.25×10^{-05}	1.138×10^{-08}	3.703×10^{-13}
Pb	$1.006 \times 10^{+05}$	5.61×10^{-05}	1.577×10^{-08}	8.841×10^{-13}
Sb	$1.089 \times 10^{+05}$	4.52×10^{-05}	3.597×10^{-09}	1.625×10^{-13}
Sn	$8.727 \times 10^{+04}$	3.86×10^{-05}	1.686×10^{-07}	6.510×10^{-12}
Th	$1.561 \times 10^{+05}$	1.00×10^{-04}	1.008×10^{-10}	1.007×10^{-14}
U	$1.963 \times 10^{+05}$	7.68×10^{-05}	1.000×10^{-10}	7.679×10^{-15}
Hf	$1.706 \times 10^{+05}$	3.46×10^{-05}	1.001×10^{-10}	3.462×10^{-15}
Mo	$1.317 \times 10^{+05}$	2.86×10^{-05}	1.595×10^{-10}	4.563×10^{-15}
Nb	$1.561 \times 10^{+05}$	3.28×10^{-05}	1.008×10^{-10}	3.301×10^{-15}
Sr	$7.970 \times 10^{+04}$	1.03×10^{-04}	6.519×10^{-07}	6.716×10^{-11}
Ta	$1.772 \times 10^{+05}$	2.77×10^{-05}	1.000×10^{-10}	2.771×10^{-15}
Y	$1.518 \times 10^{+05}$	5.54×10^{-05}	1.016×10^{-10}	5.628×10^{-15}
Zn	$1.046 \times 10^{+05}$	3.20×10^{-05}	7.707×10^{-09}	2.466×10^{-13}
Fe	$1.504 \times 10^{+05}$	2.63×10^{-05}	1.021×10^{-10}	2.686×10^{-15}

[a] The intercept of discrimination line has been included.

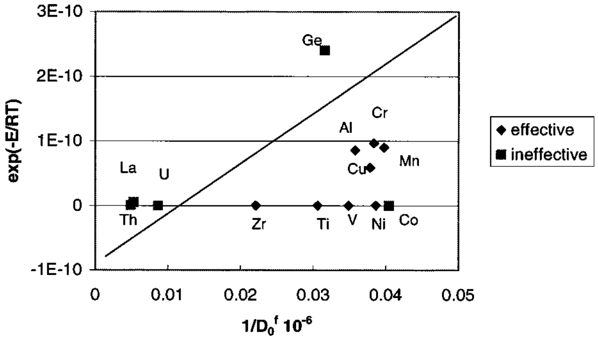

Figure 3. The correlation between the pre-exponent factor (inversion), activation energy item and additive effects. Most of points representing ineffective additives, whose Y values are too large, are not shown.

$$C_{\text{M-Zn}_{12}} = \frac{\Delta E_{2p,\text{M-Zn}_{12}} - \Delta E_{2p,\min}}{\Delta E_{2p,\max} - \Delta E_{2p,\min}} \times 0.6 + 0.2 \tag{6}$$

where C stands for the chemical shift value being normalized. Then the preexponential factor of M-Zn_{12} D_f^0 (M-Zn_{12}) can be obtained by

$$D_f^0(\text{M-Zn}_{12}) = 3.2 \times 10^{-5} \frac{C_{\text{ZnZn}_{12}}}{C_{\text{M-Zn}_{12}}} \text{ m}^2 \text{ s}^{-1} \tag{7}$$

The activation energy E_a and the preexponential fact D_f^0 (M-Zn_{12}) were listed in Table 2.

To correlate the additive effects to the diffusion coefficients, Figure 3 is constructed where the exponential term $\exp[-E(\text{M-Zn}_{12})_a/RT]$, and the inversion of the

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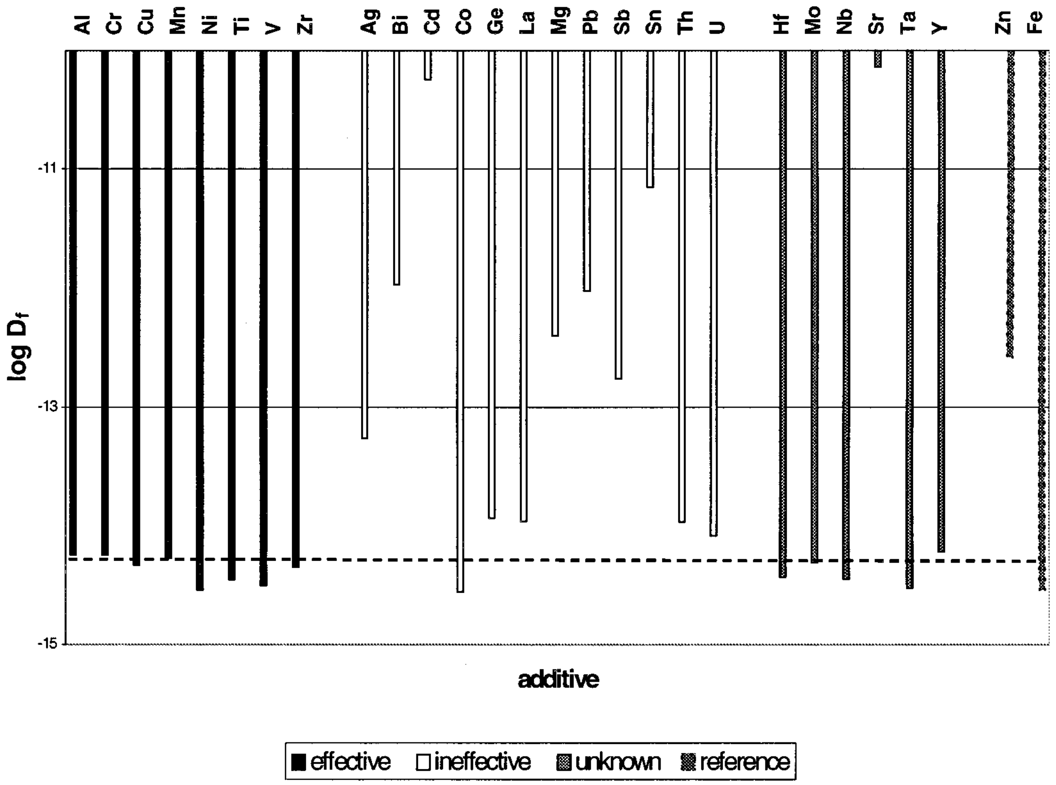

Figure 4. The zinc diffusion coefficients under the influence of additives.

preexponential term $1/D_f^0$, are taken as the Y and X axis, respectively. A discriminating line that best separates the two types of additives is obtained

$$Y = 5.5 \times 10^{-15} X - 10^{-10} \quad (8)$$

The slope of the above line (5.5×10^{-15}) has the same unit as that of the diffusion coefficient. To identify the critical zinc diffusion coefficient value that best separates the two types of additives, the Y axis is transferred by $Y + 10^{-10}$ to make the discriminating line go through the origin in Figure 3. The newly transferred Y values (which are the exponent terms) are listed in the forth column of Table 2. The so calculated zinc diffusion coefficients D_f (with the presence of various additives) are showed in the last column of Table 2 and in Figure 4. The critical zinc diffusion coefficient is 5.5×10^{-15} m^2 s^{-1}, below which it may be an effective additive. Meanwhile, the calculated zinc diffusion coefficient at temperature 673 K with no additives, 2.5×10^{-13} $m^2 s^{-1}$, is very close to the experimental value, 2.6×10^{-13} m^2 s^{-1}.[23]

3.4. Predictions of Additive Effects. Two methods are obtained for the prediction of additive effects, the first is by the discrimination function $f(\Delta E_{2p}, E_b)$, based on binding energy and chemical shift of additives, and the second is by the zinc diffusion coefficient calculation (under the influence of additives). By both methods, additives of Hf, Ta, Nb, and Mo are predicted effective, while those of Sr and Y are ineffective. But Y is very close to the boundary zone that separates the two types of additives, so further study for Y is suggested.

For the additive of Co, such as that in the previous study,[5] which is based on experimental data only, discrepancies between the model predictions and experiments are also observed in the present research, which is based on data of first-principles calculation. Since the reported ineffectiveness of Co is made based on two experimental points only,[4] furthermore, the neighbor transition metallic elements of Co in the chemical element table are all effective additives, it is really difficult to explain why Co becomes an exception. More experiments on Co additive are suggested.

For Cu additive, there exist ambiguous experimental results. Different observations asserted either Cu ineffective[2] or effective.[24,25] The latter is supported by our predictions.

In addition, it is worth notice that since the results are based on the assumption of associates the atoms of alloying additives have to be perfectly dissolved in the zinc bath. This argument is also supported by the study of aluminum additive,[1] which emphasized the importance of the additive dissolving process.

It is further noticed that the present conclusions on zinc diffusion coefficients may be used in the design of binary or ternary additives although they were made based on the study of single additive systems. The associates contain only the zinc and additive elements with no Fe atoms. Therefore, a zinc-binary or zinc-ternary additive system (Fe free) may be set up to measure the zinc diffusion coefficients which may indicate if the candidates are effective or ineffective for zinc galvanizing.

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(25) Rädeker, W.; Peters, F.; Frieche, W. In *Proceedings of the 6th International Conference on Hot Dip Galvanizing, Interlaken*; European General Galvanizers Association, Edited by Zinc Develop., London, England, 1961; p 238.

Table 3. The Calculated Results on the Relative Stability of the Icosahedral M-Zn_{12} to Three Low Coordinate Cluster Models (M-Zn_4, M-Zn_6, and M-Zn_8)

	tetrahedron M-Zn_4			octahedron M-Zn_6			hexahedron M-Zn_8		
M	d/nm	E_b/hartree	ΔE/kJ/mol	d/nm	E_b/hartree	ΔE/kJ/mol	d/nm	E_b/hartree	ΔE/kJ/mol
Al	0.2657	−0.14044	240.3	0.2760	−0.18663	271.3	0.2657	−0.24252	213.9
Cr	0.2605	−0.12723	269.7	0.2471	−0.20331	222.1	0.2605	−0.28271	103.1
Cu	0.2424	−0.15088	229.9	0.2454	−0.20858	230.6	0.2424	−0.26229	179.0
Mn	0.2545	−0.13526	251.7	0.2366	−0.21411	196.9	0.2545	−0.28797	92.4
Ni	0.2362	−0.25212	246.1	0.2367	−0.32683	202.1	0.2362	−0.38275	144.7
Ti	0.2694	−0.21031	321.3	0.2641	−0.28941	265.8	0.2694	−0.37522	129.9
V	0.2635	−0.21739	303.6	0.2510	−0.29977	239.5	0.2635	−0.38507	105.0
Zr	0.2648	−0.21728	322.7	0.2740	−0.29914	260.0	0.2648	−0.38610	121.1
Ag	0.2608	−0.12535	153.7	0.2648	−0.17304	180.7	0.2608	−0.21636	156.4
Bi	0.2974	−0.12543	41.6	0.3082	−0.15783	108.8	0.2974	−0.19055	112.3
Cd	0.2883	−0.01354	139.4	0.3081	−0.04700	203.7	0.2883	−0.09757	160.4
Co	0.2373	−0.24079	260.2	0.2365	−0.32640	187.6	0.2373	−0.38675	118.6
Ge	0.2608	−0.14658	177.9	0.2706	−0.18748	222.8	0.2608	−0.23196	195.4
La	0.3127	−0.19887	213.2	0.3083	−0.25540	217.0	0.3127	−0.32255	130.1
Mg	0.2871	−0.06627	216.4	0.3081	−0.10343	271.0	0.2871	−0.16190	206.9
Pb	0.2998	−0.12453	49.3	0.3038	−0.15931	110.2	0.2998	−0.19458	107.0
Sb	0.2835	−0.12854	105.8	0.2952	−0.16345	166.3	0.2835	−0.19970	160.5
Sn	0.2835	−0.05762	118.8	0.2918	−0.09699	167.7	0.2835	−0.13655	153.2
Th	0.3126	−0.19249	314.4	0.3083	−0.25602	299.8	0.3126	−0.33429	183.7
U	0.3041	−0.27887	408.9	0.2989	−0.34101	397.9	0.3041	−0.42789	259.2
Sr	0.3638	−0.05891	383.1	0.3579	−0.09183	288.8	0.3638	−0.13140	128.7
Ta	0.2615	−0.22981	296.2	0.2573	−0.34072	178.4	0.2615	−0.44013	45.7
Hf	0.2725	−0.21038	316.8	0.2675	−0.30430	221.9	0.2725	−0.39933	74.6
Mo	0.2833	−0.12532	55.0	0.2534	−0.22817	120.8	0.2833	−0.31279	106.3
Nb	0.2662	−0.19138	384.8	0.2647	−0.28551	245.8	0.2662	−0.37567	74.3
Y	0.2998	−0.19229	280.5	0.2926	−0.25768	261.0	0.2998	−0.33227	154.6
Zn	0.2656	−0.07395	214.4	0.2646	−0.12094	243.2	0.2656	−0.17288	196.2
Fe	0.2425	−0.19358	265.7	0.2365	−0.28193	185.9	0.2425	−0.34807	101.7

4. Conclusions

The DFT calculations of 26 M-Zn_{12} clusters that simulate the zinc associates in hot-dip galvanizing have been carried out to investigate the additive effects on controlling coating thickness. This study further confirms the previous reached conclusions that additives behaviors with regards to coating thickness are attributed to both the strong binding energy of the associate of zinc with additives and the electronic charge shift from zinc to additives. A discrimination function $f(\Delta E_{2p},E_b)$ which has the energy scale and a critical zinc diffusion coefficients D_f (under the influence of additives) have been generated. They are used in the prediction of additive behaviors of Hf, Ta, Nb, Mo, Sr, and Y. The importance of additive dissolving process is also highlighted. And finally it is suggested that it may be possible to predict the behaviors of binary or ternary additives based on the zinc diffusion capabilities in the correspondent Fe free systems.

Appendix

The relative stabilities compared of the tetrahedral M-Zn_4, octahedral M-Zn_6, and hexahedral M-Zn_8 to the stability of the icosahedral M-Zn_{12}, is measured by the dissociation energy of M-Zn_{12}, ΔE, which is defined as follows:

$$\Delta E = E_b(\text{M-Zn}_8) + E_b(\text{Zn}_4) - E_b(\text{M-Zn}_{12}) \quad \text{(A1)}$$

$$\Delta E = E_b(\text{M-Zn}_6) + E_b(\text{Zn}_6) - E_b(\text{M-Zn}_{12}) \quad \text{(A2)}$$

$$\Delta E = E_b(\text{M-Zn}_4) + E_b(\text{Zn}_8) - E_b(\text{M-Zn}_{12}) \quad \text{(A3)}$$

where $E_b(\text{M-Zn}_x)$ and $E_b(\text{Zn}_x)$ represent the binding energy of M-Zn_x and Zn_x, respectively. The tetrahedral Zn_4, octahedral Zn_6, and hexahedral Zn_8 are optimized to obtain their equilibrium interatomic distances, which are 0.2722, 0.2857, and 0.2618 nm, respectively, and their binding energies, which are −0.07047, −0.10453, and −0.16250 hartree, respectively. The calculated results are listed in Table 3. The related data for icosahedral M-Zn_{12} can be found in Table 1 of the text. The calculated results show that the dissociation energies are all positive, indicating that the configuration of icosahedral M-Zn_{12} is more stable compared to other three configurations.

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